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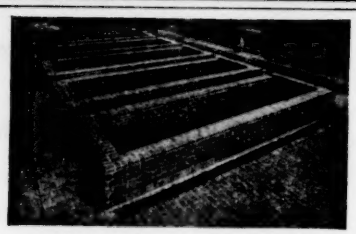

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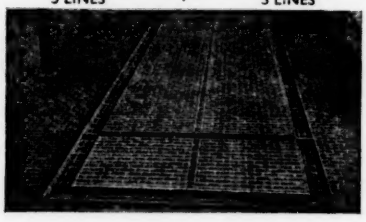

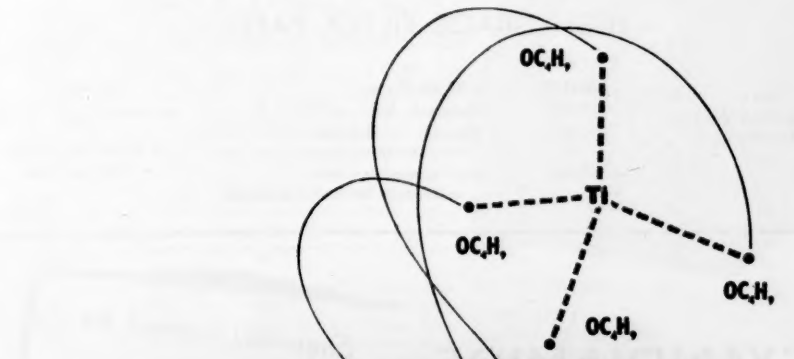


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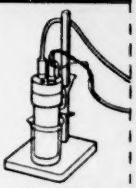

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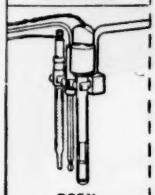

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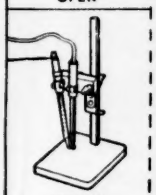

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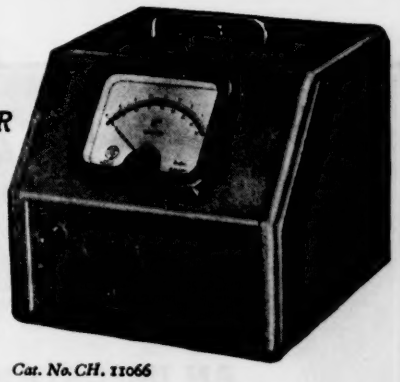

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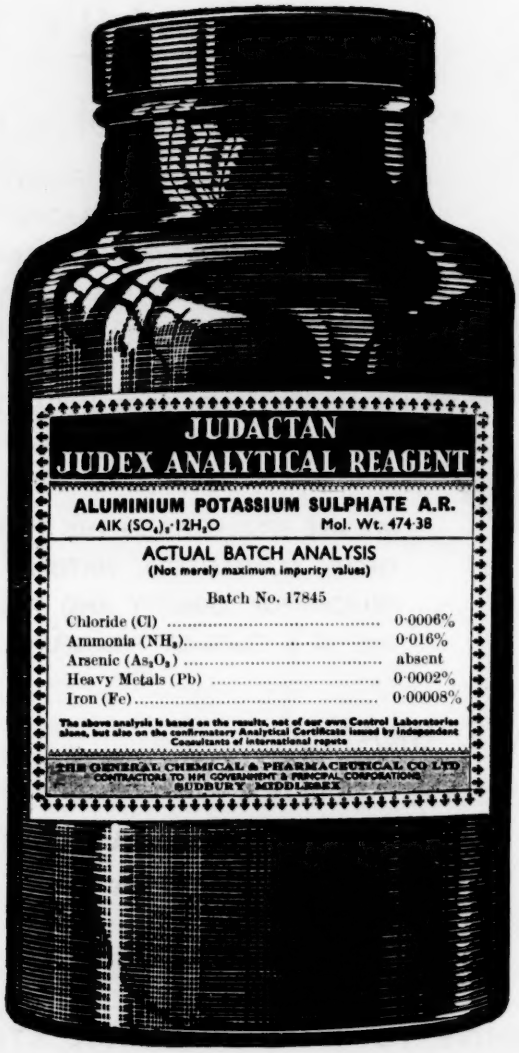
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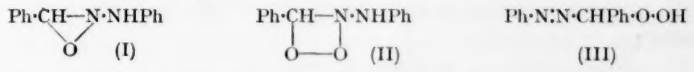
## 513. *The Oxidation of Phenylhydrazones with Perphthalic Acid. Part I.*

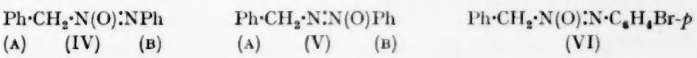
By B. M. Lynch and K. H. Pausacker.

It has been shown that benzaldehyde phenylhydrazone reacts with perphthalic acid forming benzylazoxybenzene. Similar oxidation of a number of substituted benzaldehyde phenylhydrazones has also been investigated.

Bergmann, Ulpts, and Witte (*Ber.*, 1923, **56**, 679) found that benzaldehyde phenylhydrazone, $C_{13}H_{12}N_2$, was oxidized by perbenzoic acid (we have used perphthalic acid) to a compound, $C_{13}H_{12}ON_2$, m. p. 201°, to which they assigned structure (I). This structure resembles that (II) proposed by Busch and Dietz (*Ber.*, 1914, **47**, 3277) for the autoxidation




product of benzaldehyde phenylhydrazone, which has since been shown to be (III) (Pausacker, *J.*, 1950, 3478; Criegee and Lohaus, *Chem. Ber.*, 1951, **84**, 219). By analogy, it might be expected that the per-acid oxidation product would be Ph·N:N·CHPh·OH, which would immediately rearrange forming *N*-benzoyl-*N'*-phenylhydrazine. However, as this has m. p. 168°, it is obviously not the product (cf. Bergmann, Ulpts, and Witte, *loc. cit.*). Two other simple possibilities are benzylazoxybenzene (IV) and ω-phenylazoxytoluene (V).



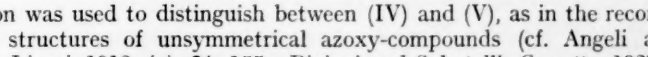

The infra-red absorption spectrum of the per-acid oxidation product (kindly measured by courtesy of Professor J. D. Roberts of the Massachusetts Institute of Technology) has strong bands at 6·73 and 6·91 μ, and less intense bands at 7·57 and 7·67 μ. This indicates the possibility of an azoxy-structure as Langley, Lythgoe, and Rayner (*J.*, 1952, 4193) found that characteristic vibrations of the azoxy-group (in azoxymethane) are in the 6·55 and the 7·45 μ region and that C–H deformation modes occur at 7·24 and 6·96 μ. Furthermore, no significant absorption is present in the regions 2·88—3·28 and 5·89—6·00 μ, indicating the absence of –NH– and >C=N– groups respectively.

Confirmatory evidence results from reduction of the per-acid oxidation product to benzaldehyde phenylhydrazone in excellent yield by lithium aluminium hydride. This is in accord with Brown and Nystrom's finding (*J. Amer. Chem. Soc.*, 1948, **70**, 3738) that the reduction of azoxybenzene by lithium aluminium hydride yields azobenzene quantitatively.

As would be expected on the basis of the azoxy-structure, neither acetophenone nor benzaldehyde *N*-methyl-*N*-phenylhydrazone could be oxidized by perphthalic acid to a product containing an oxygen atom; some reaction did, however, take place (as shown by the titration of "active" oxygen), and it is intended to investigate these reactions in detail.

Bromination was used to distinguish between (IV) and (V), as in the recorded elucidations of the structures of unsymmetrical azoxy-compounds (cf. Angeli and Valori, *Atti R. Accad. Lincei*, 1912, (v), **21**, 155; Bigiavi and Sabatelli, *Gazzetta*, 1927, **57**, 559). Bromination readily occurred and this indicates that structure (IV) is correct as the benzene ring (B) in (IV) would be the only one that would be substituted readily. The bromination product was assigned structure (VI) as it was found to be identical (mixed m. p.) with the per-acid oxidation product of benzaldehyde *p*-bromophenylhydrazone.

If the mechanism of the per-acid oxidation is assumed to be:



then structure (IV) is also more likely than (V) since the nitrogen atom attached directly to the benzyl group in (VII) is the more basic, and it has been shown (Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692) that per-acids are electrophilic reagents. Furthermore, (IV) would be stabilized by resonance between the azoxy-group and the phenyl group (B) whereas this is not possible in (V).

A number of nuclear-substituted benzaldehyde phenylhydrazones have been oxidised by perphthalic acid and the yields determined, as it is intended to investigate this reaction kinetically.

Langley, Lythgoe, and Rayner (*loc. cit.*) have stated that they have investigated the compound obtained by the action of perbenzoic acid on benzaldehyde phenylhydrazone and " whatever its structure, it was not the expected azoxy-compound." No experimental evidence is given to support this statement. However, these authors found that primary aliphatic azoxy-compounds reacted with mineral acid to yield a carboxylic acid and a hydrazine. This further supports structure (IV) as Bergmann, Ulpts, and Witte (*loc. cit.*) found that the per-acid oxidation product reacts with acetic acid forming *N*-benzoyl-*N'*-phenylhydrazine.

## Experimental

(M. p.s are corrected. Microanalyses are by Dr. W. Zimmermann.)

*Per-acid Oxidation of Substituted Benzaldehyde Phenylhydrazones.*—Perphthalic acid ($5 \times 10^{-3}$ mole) in ether (20 ml.) was added to the appropriate benzaldehyde phenylhydrazone ($5 \times 10^{-3}$ mole). After 2 days the product was filtered off. Phthalic acid was removed from the filtrate by extraction with sodium hydrogen carbonate solution, and a further amount of product obtained by evaporation of the ether under reduced pressure. Yields, m. p.s, and analyses of the *azoxy*-compounds are shown in the following Table; primed numerals (2', etc.) refer to positions in the benzene ring B.

| Substituent | Yield (%) | M. p. (with decomp.) | Solvent | Found (%) C | H | N | Cl |
|---|---|---|---|---|---|---|---|
| — | 96 | 201° | Pyridine | — | — | — | — |
| 3-Me | 94 | 177 | ,, | 74·8 | 5·9 | 12·5 | — |
| 4-Me | 98 | 180 | ,, | 74·2 | 6·0 | 12·3 | — |
| 3'-Me | 98 | 172 | Ethyl acetate | 74·1 | 6·1 | 12·2 | — |
| 4'-Me | 96 | 187 | Ethanol–pyridine | 74·2 | 5·8 | 12·4 | — |
| | $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2; N, 12·4%. | | | | | | |
| 3-OMe | 100 | 173 | Ethanol–pyridine | 69·7 | 5·7 | 11·7 | — |
| 4-OMe | 94 | 176 | ,, | 69·4 | 5·8 | 11·8 | — |
| 3'-OMe | 92 | 168 | ,, | 69·4 | 5·8 | 11·7 | — |
| 4'-OMe | 96 | 173 | ,, | 69·5 | 5·5 | 11·8 | — |
| | $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8; N, 11·6%. | | | | | | |
| 3-Cl | 95 | 186·5 | Ethanol–pyridine | — | — | 11·4 | 14·4 |
| 4-Cl | 97 | 182·5 | ,, | — | — | 11·3 | 14·4 |
| 3'-Cl | 97 | 163·5 | Pyridine | — | — | 11·5 | 13·9 |
| 4'-Cl | 99 | 186·5 | ,, | — | — | 11·1 | 14·3 |
| | $C_{13}H_{11}ON_2Cl$ requires N, 11·4; Cl, 14·4%. | | | | | | |
| 3-$NO_2$ | 90 | 169 | Ethanol–pyridine | 60·7 | 3·9 | 16·1 | — |
| 4-$NO_2$ | 94 | 135 | ,, | 60·6 | 4·4 | 16·5 | — |
| 3'-$NO_2$ | 90 | 192 | Ethyl acetate | 61·0 | 4·5 | 16·4 | — |
| | $C_{13}H_{11}O_3N_3$ requires C, 60·7; H, 4·3; N, 16·3%. | | | | | | |
| 4'-Br | 97 | 203 | Pyridine | 53·9 | 3·8 | 9·3 | — |
| | $C_{13}H_{11}ON_2Br$ requires C, 53·6; H, 3·8; N, 9·6%. | | | | | | |
| Ph·CH:N·NH·$C_{10}H_7$-$\beta$ | 95 | 172·5 | Ethyl acetate | 77·6 | 5·0 | 10·8 | — |
| | $C_{17}H_{14}ON_2$ requires C, 77·9; H, 5·4; N, 10·7%. | | | | | | |

*Reduction of* (IV) *with Lithium Aluminium Hydride.*—The azoxy-compound (IV) (0·45 g.) in dry ether (500 ml.) was refluxed (8 hr.) with lithium aluminium hydride (0·05 g., in 50 ml. of dry ether). Excess of hydride was destroyed with moist ether (100 ml.), the aluminium hydroxide filtered off, and the filtrate dried ($Na_2SO_4$). Upon evaporation and crystallization

from aqueous ethanol, benzaldehyde phenylhydrazone (0·35 g.) was obtained, having m. p. 156—157°, and mixed m. p. with authentic material 157—158°.

*Bromination.*—Bromine (3 g.) in pyridine (20 ml.) was added to the azoxy-compound (IV) (1·25 g.) in pyridine (100 ml.), and the mixture refluxed for 10 min. and then set aside for 3 days. The precipitate (1·6 g.) formed on addition of ethanol (100 ml.) was filtered off and crystallized from pyridine. It had m. p. 202—203° (decomp.), mixed m. p. with (IV) 190—194°, and mixed m. p. with (VI) 202—203° (decomp.).

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## 514. *Trimethylgallium. Part II.* Reactions with Hydroxy- and Similar Compounds.*

By G. E. COATES and R. G. HAYTER.

Trimethylgallium forms weak co-ordination compounds with acetone and methyl cyanide, but with methanol, methanethiol, methaneselenol, and acetic acid elimination of methane gives dimeric products, *e.g.*, $(Me_2Ga{\cdot}SMe)_2$. The methoxy-derivative is unaffected by trimethylamine, whereas the others are split reversibly, *e.g.*, to $MeS{\cdot}GaMe_2{\cdot}\overset{-}{N}\overset{+}{M}e_3$. Similar dimeric compounds are obtained from phenol, *p-tert.*-butylphenol, *p*-chlorophenol, thiophenol, and selenophenol; all these products are split by trimethylamine. Acetylacetone and salicylaldehyde give monomeric products. 2-Dimethylaminoethanol gives a dimeric cyclic compound in which the oxygen atoms appear to be co-ordinated to gallium in preference to the nitrogen atoms.

WHEREAS the final products of the reactions of many organometallic compounds with a variety of substances have been investigated, usually after the reaction mixture has been decomposed with water, the primary reaction products have received little attention. They are the subject of the present paper for the special case of trimethylgallium, whose characteristic reaction is the expansion of the covalency of the gallium atom to four by co-ordination to a donor atom. Any subsequent reaction appears to depend on the presence of reactive hydrogen in the resulting co-ordination compound (other possibilities, such as the presence of reactive halogen, have not yet been investigated).

With methyl cyanide, a weak co-ordination compound is formed, which is fully dissociated in the vapour state at 100°/90 mm., and no further reaction occurs. On the other hand, with acetone, which is more acidic, a 1 : 1 co-ordination compound is again formed, but between 60° and 90° one mol. of methane is evolved, giving a non-volatile product $Me_2Ga{\cdot}OC_3H_5$. The latter, possibly an *iso*propenyl compound, evolves a little more methane at 170° and evidently then decomposes extensively to an involatile orange-yellow mass.

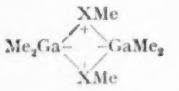
Compounds containing a still more acidic hydrogen atom give methane directly and products which usually contain two gallium atoms. In Part I* it was shown that with ammonia, methylamine, and dimethylamine, trimethylgallium forms co-ordination compounds which evolve a mol. of methane when heated, giving dimeric products, *e.g.*, $(Me_2Ga{\cdot}NH_2)_2$, to which cyclic structures were assigned. The reactions between trimethylgallium and compounds containing hydrogen bonded to oxygen, sulphur, and selenium, all weaker donor atoms (to gallium) than nitrogen, have now been studied and, although a co-ordination compound is likely to be the initial product, in all cases methane evolution occurs at or below room temperature.

Methanol, methanethiol, and methaneselenol give products which are sufficiently volatile to be vaporised completely and hence to allow their molecular weights to be determined in the gas phase. They are dimeric † like the products from ammonia and methyl- and

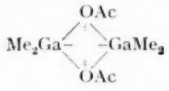
* Part I, *J.*, 1951, 2003.

† One of the corresponding aluminium compounds, $AlMe_2{\cdot}OMe$, is described as dimeric by Wiberg and Stecher (FIAT Review, 1939—46, Inorganic Chemistry, Part II, p. 160) and as trimeric by Brown and Davidson (*J. Amer. Chem. Soc.*, 1942, **64**, 316).

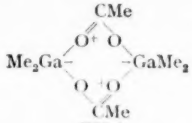
dimethyl-amine, and show no sign of dissociation at temperatures and pressures at which the simpler co-ordination compounds $Me_3Ga{\cdot}OMe_2$, $Me_3Ga{\cdot}SMe_2$, and $Me_3Ga{\cdot}SeMe_2$ are almost fully dissociated. They are assigned cyclic structures (I)—(III), since no other formulation appears reasonable. These cyclic structures are compatible with their high




(I; X = O) (II; X = S) (III; X = Se)




(IV)




(IV*a*)

stability, since their dissociation would involve the breaking of two bonds, whereas the dissociation of the simple co-ordination compounds of trimethylgallium involves only one. In fact no evidence for dissociation of any of the above compounds in the gaseous phase was obtained from vapour-density measurements up to 170°. The heats of co-ordination of dimethyl ether, sulphide, and selenide with trimethylgallium are from 8 to 10 kcal./mole (Part I). Electropositive substituents such as methyl increase the donor properties of a donor atom and diminish the acceptor properties of an acceptor atom. The acceptor nature of the gallium atom in (I) should be greater than in $Me_3Ga{\cdot}OMe_2$, since it is bonded to two electronegative oxygen atoms and only two electropositive methyl groups instead of one and three respectively. Similarly the oxygen in (I) is bonded to two electropositive gallium atoms and one methyl group instead of one and two. Consequently the heat of dissociation of (I) should be very considerably more than twice that of $Me_3Ga{\cdot}OMe_2$, *i.e.*, well over 20 kcal./mole, in agreement with the observed lack of dissociation.

Acetic acid reacts vigorously with trimethylgallium giving methane and dimethylgallium acetate, which is dimeric (in acetone solution) and is therefore assigned the structure (IV). Evidently even the rather electronegative acetyl group does not sufficiently depress the donor nature of the oxygen to prevent dimerisation. An alternative structure (IV*a*) would allow resonance in the carboxy-group,* which would increase stability. The authors have no means for distinguishing between (IV) and (IV*a*) by, for example, infra-red measurements. Some of the properties of these compounds are given in Table I.

TABLE 1.

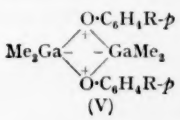
| Compound | M. p. | B. p. (extrap.) | *A* * | *B* | $L_v$ † | Trouton const. | Temp. range |
|---|---|---|---|---|---|---|---|
| $Me_3Ga{\cdot}NC{\cdot}Me$ ..... | 24·8—25·2° | 120° | 2342 | 8·840 | 10·7 | 27·3 | 25—80° |
| $Me_3Ga{\cdot}OCMe_2$ ..... | — | 104 | 2648 | 9·896 | 12·1 | 32·1 | 20—55 |
| $(Me_2Ga{\cdot}OMe)_2$ ..... | 24·5—24·7 | 187 | 2903 | 9·187 | 13·3 | 28·8 | 40—150 |
| $(Me_2Ga{\cdot}SMe)_2$ (s) ... | 113·3—113·7 | — | 5800 | 15·00 | 26·6 ‡ | — | 80—110 |
| ,, (l) ... | — | 243 | 2990 | 8·679 | 13·7 | 26·6 | 115—170 |
| $(Me_2Ga{\cdot}SeMe)_2$ (l) ... | 119—120 | — | 3450 | 9·63 | 16 | — | 120—140 |
| $(Me_2Ga{\cdot}O{\cdot}CO{\cdot}Me)_2$ ... | 162·0—162·3 | 216 | 4704 | 12·50 | 21·6 ‡ | — | 90—162 |

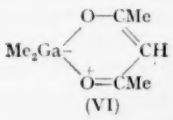
* $\text{Log}_{10}$ (v. p.)$_{mm.} = -(A/T) + B$. † Latent heat of evaporation, kcal./mole.
‡ Latent heat of sublimation.

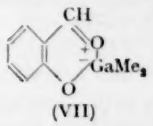
Phenol and *p-tert.*-butylphenol also give methane and dimeric products (V; R = H and $CMe_3$ respectively). The combined effect of a phenol group and a *p*-chlorine atom, however, depresses the donor character of oxygen more extensively, since molecular-weight measurements on the product from *p*-chlorophenol indicate an equilibrium between monomer and dimer. Similarly, thio- and seleno-phenol give analogous dimeric compounds. *p*-Chlorothiophenol gives a dimer $(Me_2Ga{\cdot}S{\cdot}C_6H_4Cl)_2$ with indication of partial dissociation into monomer in dilute benzene solution. Although thiols and selenols are more acidic than the corresponding alcohols and phenols in aqueous or hydroxylic media, thiophenol and selenophenol react much more slowly than phenol with trimethylgallium in ether.

* The authors are indebted to a referee for suggesting this point.

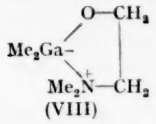
Monomeric compounds (VI) and (VII) are obtained from trimethylgallium and acetylacetone and salicylaldehyde. The former is volatile and similar to the thallium compound $Me_3Tl{\cdot}C_5H_7O_2$ (Menzies, Sidgwick, Cutcliffe, and Fox, *J.*, 1928, 1288). These compounds

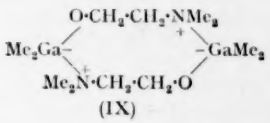

(V)

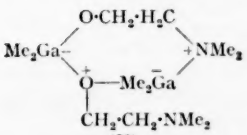

(VI)

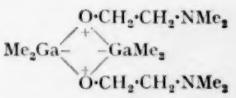

(VII)

may be monomeric because two donor atoms are available in the reacting molecule, or because a conjugated system is formed (VII is bright yellow). The latter effect is probably the more important since 2-dimethylaminoethanol does not give the expected monomeric product (VIII) but a dimer, for which structures (IX)—(XI) are feasible. This


(VIII)


(IX)


(X)


(XI)

compound immediately forms a methiodide on addition of methyl iodide to its benzene solution, suggesting the presence of tercovalent nitrogen; thus the ten-membered ring structure (IX) is improbable. The methiodide is very hygroscopic, easily hydrolysed, and not easy to purify and analyse. The iodine content, however, was a few units per cent. short of that calculated for a dimethiodide and far too large for a monomethiodide; hence the four-membered ring structure (XI) is preferred. The formation of (XI) rather than (VIII) is remarkable since nitrogen is a considerably stronger donor than oxygen, and suggests that gallium has a particularly high tendency to form four-membered rings with oxygen.

Although no direct measurement of the heats of dissociation of these compounds into monomers has been possible, on account of their high stability, some information about relative stabilities is provided by their reaction with trimethylamine. Thus, one of the most stable compounds, the methoxide (I), does not react with trimethylamine, whereas the monomeric *p*-chlorophenoxide forms a 1 : 1 co-ordination compound whose dissociation pressure is only about 1 mm. at 20°. The dissociation pressure at 20° of the trimethylamine adducts of most of the compounds prepared are given in Table 2. A low dissociation

TABLE 2. *Dissociation pressures at* 20° *of* $Me_2\bar{G}aR{\cdot}\dot{N}Me_3$.

| R | *P* (mm.) | R | *P* (mm.) | R | *P* (mm.) |
|---|---|---|---|---|---|
| OMe | No adduct | $O{\cdot}C_6H_4Bu^t$-*p* | 14 | SPh [a] | 0·4 (m. p. 51°) |
| SMe [a] | 10·3—10·4 (m. p. 26·0—26·2°) | OPh | 6·1 (m. p. 39—40°) | SePh | 0·1—0·2 (m. p. 48—50°) |
| SeMe [b] | 4·5 (m. p. 29·8—30·0°) | $O{\cdot}C_6H_4Cl$-*p* | 1·5 | $O{\cdot}C_6H_4{\cdot}CHO$-*o* | 11 |

$\Delta H$ (dissociation): $a = 7{\cdot}5$; $b = 6{\cdot}6$; $c = 9{\cdot}3$ kcal./mole.

pressure indicates that trimethylamine successfully competes with R as a donor to gallium; thus, for a group of similar compounds in which entropy changes would be alike, the donor properties of the group R should be in the same order as the dissociation pressures. Table 2 thus indicates that: (*a*) the order of donor character is O > S > Se, a result in contrast to that found in Part I (O > Se > S), for co-ordination between $Me_3Ga$ and $OMe_2$, $SMe_2$, and $SeMe_2$ (the difference between S and Se is small and may easily be due to entropy effects);

(*b*) substitution of phenyl for methyl diminishes the dissociation pressure and thus also diminishes the donor nature of the atom concerned, *e.g.*, R = SMe, $p$ = 10 mm., while for R = SPh, $p$ = 0·4 mm.; and (*c*) substitution of an electropositive radical ($Bu^t$) in a phenoxy-group increases the donor character of the oxygen, while an electronegative radical (Cl) decreases it. Effects (*b*) and (*c*) illustrate the well-known effect of the electronegativity of substituents bonded to a donor atom on its donor character.

Neither the acetylacetone derivative (VI) nor the dimethylaminoethanol derivative (XI) reacts with trimethylamine, but the salicylaldehyde derivative (VII) forms an unstable adduct (dissociation pressure 11 mm. at 20°; m. p. 56—67° with decomp.).

## Experimental

All the compounds described were prepared in a vacuum-apparatus, but the less volatile ones were purified by crystallisation in normal apparatus with care to exclude water. Trimethylgallium was prepared as described in Part I. The other reagents were prepared and purified by established methods, except 2-dimethylaminoethanol, which required careful drying by three distillations over barium oxide, and methaneselenol, which was prepared by the reduction (by sodium in liquid ammonia) of dimethyl diselenide (Coates, this vol., paper no. 575) and was purified by fractionation in the vacuum-apparatus.

*Trimethylgallium–Methyl Cyanide.*—Trimethylgallium (17·7 N-c.c.) and methyl cyanide (17·7 N-c.c.) were condensed in the high-temperature bulb (see Part I). A mild reaction occurred when the former melted, and the addition compound, m. p. 24·8—25·2°, crystallised. No methane was formed. The v. p. was measured from 20° to 80°. Above 85° the bulb contained gas only. The vapour volume was 33·0, 33·5, 33·8, and 34·0 N-c.c. at 90°, 100°, 110°, and 120°, indicating almost complete dissociation. No methane was formed even at 100°, the compound being unchanged on cooling to room temperature.

*Trimethylgallium–Acetone.*—The components (17·5 N-c.c. of each) gave a liquid, v. p. 8 mm./22°, with no evolution of methane. The *product* froze to a homogeneous crystalline mass below room temperature. The v. p. was measured between 20° and 55°. It was not possible to measure the density of the vapour since reaction occurred at an appreciable rate at 50° and above, with deposition of a white solid and formation of methane. The bulb was heated to 90° for 10 min., then cooled to room temperature, and methane (17·8 N-c.c.) was removed. The residue, which must have the composition $Me_2Ga{\cdot}OC_3H_5$, was non-volatile at room temperature. Further heating at 170° (10 min.) gave a further 5·7 N-c.c. of methane (0·33 mole per g.-atom of gallium), and the solid became orange-yellow.

*Tetramethyl-μμ′-dimethoxydigallium* * (I).—Trimethylgallium (28·2 N-c.c.) and methanol (28·2 N-c.c.) were condensed in the high-temperature bulb at −183°. Warming caused vigorous gas evolution as soon as the trimethylgallium melted; a colourless liquid was formed, which later crystallised. The vessel was again cooled in liquid oxygen, and the gas, identified as methane (v. p. at −183°), was quantitatively pumped into a gas burette (28·1 N-c.c.). The composition of the residue was therefore $Me_2Ga{\cdot}OMe$ (which requires $CH_4$ 28·2 N-c.c.). The compound melted at 24·5—24·7° and became entirely gaseous at 128°. Between 140° and 150° the volume of the vapour (reduced to N.T.P.) was 13·9 N-c.c.; hence the vapour is dimeric, *i.e.*, $(Me_2Ga{\cdot}OMe)_2$. For the measurement of v. p. a larger quantity was prepared by a similar method. The compound was stable to dry air and did not react with an excess of methanol.

*Tetramethyl-μμ′-dimethoxydigallium* did not react with trimethylamine.

*Tetramethyl-μμ′-bismethylthiodigallium* (II).—Trimethylgallium (27·1 N-c.c.) and methanethiol (27·1 N-c.c.) were condensed in the high-temperature bulb at −183°. Rapid gas evolution was observed as soon as the trimethylgallium melted, but the reaction (unlike that with methanol) could be stopped by cooling in liquid oxygen. Methane (27·0 N-c.c.; identified by v. p.) was pumped from the colourless solid product (non-volatile at room temperature), which therefore had the composition $Me_2Ga{\cdot}SMe$. The v. p. was measured and is given above; at 175° the compound had entirely volatilised and at 180° and 190° its volume was 13·5 and 13·7 N-c.c. respectively, indicating a dimeric structure.

*Reaction with trimethylamine.* When the high-temperature bulb was cooled after the v.-p. measurement, the compound crystallised fairly uniformly over the glass surface. Trimethylamine (27·1 N-c.c.; 1 mole per g.-atom of gallium) was then condensed in the bulb. On warming

* On the basis of the nomenclature used in Part I, this compound could be called *cyclo*(bismethyloxonium bisdimethylgallide) (cf. *J.*, 1951, 3515).

to room temperature, the gas occupied 24·2 N-c.c.; thus only a little trimethylamine had reacted. When the bulb was warmed with the hand, the pressure rapidly decreased to 12 mm., and the white deposit liquefied and soon (at room temperature) crystallised to long needles (often 4—5 cm.) of *dimethyl(methylthio)gallium–trimethylamine*, m. p. 26·0—26·2°. When the bottom of the bulb was cooled with liquid oxygen, these needles broke into minute crystals of (II), since 27·1 N-c.c. of trimethylamine were recovered by pumping as it warmed to room temperature. The trimethylamine was replaced, the addition compound formed again, and dissociation pressures were measured up to 160°.

*Tetramethyl-μμ′-bismethylselenodigallium* (III).—Trimethylgallium (10·6 N-c.c.) and methaneselenol (10·6 N-c.c.) gave methane (10·5 N-c.c.) and a white relatively non-volatile solid. The v. p. of the latter was measured over a rather short temperature range since a little non-condensable gas was formed at > 160°; the constants given in Table I are therefore only approximate. At 155° and 160° the material had volatilised and its volume was 5·1 and 5·4 N-c.c. respectively; a very small quantity of white deposit separated during these measurements. As vapour the substance was therefore dimeric $(Me_2Ga{\cdot}SeMe)_2$.

*Reaction with trimethylamine.* Addition of trimethylamine (10·6 N-c.c.) gave results very similar to those observed with the analogous sulphur compound, but the amine was absorbed more rapidly. The addition compound, *dimethyl(methylseleno)gallium–trimethylamine*, again formed long needles, m. p. 29·8—30·0°, which lost trimethylamine when the bottom of the bulb was cooled with liquid oxygen. On pumping at room temperature, 10·4 N-c.c. of trimethylamine were recovered. The trimethylamine was replaced and the dissociation pressure measured between 30° and 90°.

*Tetramethyl-μμ′-diacetoxydigallium* (IV).—This *product*, prepared from the trimethylgallium–ether complex and acetic acid, was purified by vacuum-sublimation at 135°, forming colourless crystals, m. p. 162·0—162·3° (Found: C, 30·2; H, 5·63; Ga, 43·8%; *M*, ebullioscopic in acetone, 325, 308. $C_8H_{18}O_4Ga_2$ requires C, 30·2; H, 5·65; Ga, 44·0%; *M*, 318). It absorbs trimethylamine at room temperature forming an unstable adduct from which all the trimethylamine can be removed by pumping at room temperature.

*Tetramethyl-μμ′-diphenoxydigallium* (V; R = H).—Trimethylgallium (22 millimoles, 10% excess) was combined with a slight excess of ether and then condensed (as ether complex) on a frozen solution of phenol (19·4 millimoles) in ether (10 c.c.). Gas evolution began as the mixture warmed to about 0° and became vigorous near room temperature. The solution was removed from the vacuum-apparatus, light petroleum (b. p. 60—80°; 30 c.c.) added, and most of the ether distilled away. By next morning *tetramethyl-μμ′-diphenoxydigallium* (1·91 g., 52%) had separated as large colourless plates, m. p. 132° (Found: C, 49·8; H, 5·7; Ga, 36·0%; *M*, cryoscopic in benzene, 388, 389, 381. $C_{16}H_{22}O_2Ga_2$ requires C, 49·7; H, 5·7; Ga, 36·3%; *M*, 386). The compound is very soluble in most organic solvents. It dissolves with hydrolysis (smell of phenol) in cold water, and the solution evolves gas (probably methane) with precipitation of a white solid when heated. The solid sublimes slowly in *vacuo* at 100°.

*Reaction with trimethylamine.* Trimethylamine (24·8 N-c.c.) was condensed on tetramethyl-μμ′-diphenoxydigallium (0·161 g.). Some gas was absorbed after warming to room temperature, and considerably more at 30—40°. By a few seconds' pumping at 0°, trimethylamine (5·4 N-c.c.) was recovered; thus 19·4 N-c.c. (just under one mole per g.-atom of gallium) had reacted, forming *dimethylphenoxygallium–trimethylamine*, colourless needles, m. p. 39—40°. The dissociation pressure is 6 mm. at 20°, and 38 at 50°. All the trimethylamine could be removed by pumping, slowly at room temperature, and quickly above the m. p. of the adduct.

The following preparations were carried out by essentially the same method.

*Tetramethyl-μμ′-bis-*p-tert.*-butylphenoxydigallium* (V; R = $Bu^t$) from *p-tert.*-butylphenol, needles (from light petroleum), m. p. 92° (Found: C, 57·8; H, 7·5; Ga, 28·0%; *M*, ebullioscopic in benzene, 447. $C_{24}H_{38}O_2Ga_2$ requires C, 57·9; H, 7·6; Ga, 28·1%; *M*, 498).

*Tetramethyl-μμ′-bis-*p-*chlorophenoxydigallium*, from *p*-chlorophenol, colourless needles (from ether), m. p. 147° (Found: C, 42·5; H, 4·5; Ga, 31·1. $C_{16}H_{20}O_2Cl_2Ga_2$ requires C, 42·3; H, 4·4; Ga, 30·8%). The molecular weight, measured ebullioscopically in benzene, increased with concentration: Found: *M*, 335 (0·55% solution), 374 (1·0%), 386 (1·4%), 394 (2·0%), 399 (2·5%), 432 (3·4%). $C_{16}H_{20}O_2Cl_2Ga_2$ requires *M*, 455.

*Tetramethyl-μμ′-bisphenylthiodigallium* from thiophenol, which reacted with trimethylgallium (in ether) markedly more slowly than the phenols, colourless crystals (from light petroleum), purified by sublimation in a high vacuum at 120—125°, m. p. 143—145° (Found: Ga, 33·2%; *M*, ebullioscopic in benzene, 410, 401, 419, 420, 414. $C_{16}H_{22}S_2Ga_2$ requires Ga, 33·4%; *M*, 418). This compound was also prepared and identified by quantitative synthesis

in the high-vacuum apparatus: thiophenol (0·0715 g., *i.e.* 14·5 N-c.c.) and trimethylgallium (14·5 N-c.c.) were condensed in the " high-temperature bulb." Vigorous gas evolution was observed on warming to room temperature. Next morning methane (14·4 N-c.c.; identified by v. p. at −183°) was pumped off; the composition of the residue was thus established as $C_6H_5{\cdot}SH + Me_3Ga - CH_4$, *i.e.*, $(C_8H_{11}SGa)_x$. The product sublimed in the high-temperature bulb at 110—120°, but was not sufficiently volatile for v. p. measurements by simple methods; it absorbed trimethylamine (14·4 N-c.c.), giving *dimethylphenylthiogallium–trimethylamine*, m. p. 51°, whose dissociation pressure was measured between room temperature and 100°.

*Tetramethyl-μμ′-bisphenylselenodigallium*, from selenophenol, colourless crystals (from benzene), m. p. 136°, becoming yellow on exposure to air (hydrolysis and subsequent oxidation of selenophenol to diphenyl diselenide) (Found: Ga, 27·1%; *M*, ebullioscopic in benzene, 520, 518, 478, 491, 482, 497. $C_{16}H_{22}Ga_2Se_2$ requires Ga, 27·3%; *M*, 512).

*Tetramethyl-μμ′-bis-p-chlorphenylthiogallium*, from *p*-chlorothiophenol, small colourless needles (from benzene and light petroleum), m. p. 187—188° [Found: Ga, 28·4%; *M*, ebullioscopic in benzene, 396 (0·4% solution), 445 (0·79%), 467 (0·96%), 457 (1·26%), 486 (1·53%) 467 (1·73%). $C_{16}H_{20}Cl_2S_2Ga_2$ requires Ga, 28·8%; *M*, 487].

*Dimethylgallium–acetylacetone* (VI), from acetylacetone, colourless prisms, purified by sublimation at room temperature (v. p. 1·1 mm. at 20°), m. p. 21·8—22·0° (Found: Ga, 34·9, 35·2%; *M*, from vapour density, 203. $C_7H_{13}O_2Ga$ requires Ga, 35·1%; *M*, 199). The v. p. was measured between 32° and 130°: below 65°, $\log_{10} p_{mm.} = 9{\cdot}333 - 2722/T$; above 65°, $\log_{10} p_{mm.} = 8{\cdot}226 - 2348/T$; whence the b. p. is 166°, and the Trouton constant 24·4. This complex did not combine with trimethylamine.

*Salicylaldehyde–dimethylgallium* complex (VII) from salicylaldehyde, bright yellow deliquescent needles (from ether), purified by vacuum-sublimation at 50°, m. p. 79° (Found: Ga, 31·4%; *M*, ebullioscopic in benzene, 221, 216, 221. $C_9H_{11}O_2Ga$ requires Ga, 31·7%; *M*, 221). With trimethylamine an unstable adduct was formed, dissociation pressure 11 mm. at 20°, which melted between 56° and 67° with evolution of trimethylamine. All the latter could easily be removed by pumping at room temperature.

*Tetramethyl-μμ′-bis-2-dimethylaminoethoxydigallium* (XI), from 2-dimethylaminoethanol, colourless crystals, purified by vacuum-sublimation at 45°, m. p. 81·4° (Found: C, 38·3; H, 8·4; Ga, 36·9%; *M*, ebullioscopic in benzene, 350, 378, 349, 362, 360. $C_{12}H_{32}O_2N_2Ga_2$ requires C, 38·3; H, 8·5; Ga, 37·1%; *M*, 376). Addition of methyl iodide to its benzene solution gave a very hygroscopic white precipitate, m. p. 264—266° (decomp. with darkening above 220°). Crystallisation of the latter from moist acetone gave 2-hydroxyethyltrimethylammonium iodide, m. p. 266° (not depressed by mixture with a specimen prepared from 2-dimethylaminoethanol and methyl iodide) (Found: C, 26·0; H, 5·8; I, 54·8. Calc. for $C_5H_{14}ONI$: C, 26·0; H, 6·0; I, 55·0%). Owing to the high sensitivity of the methiodide to moisture direct analysis was difficult (Found: I, 34·9. Calc. for dimethiodide $C_{14}H_{38}O_2N_2I_2Ga_2$: I, 38·5; for the monomethiodide $C_{13}H_{35}O_2IGa_2$: I, 24·7%).

The compound (XI) did not react with trimethylamine.

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THE UNIVERSITY, BRISTOL. [*Received, March 10th*, 1953.]

## 515. *Studies in Spectroscopy. Part IV.* The Infra-red and Ultra-violet Spectra of Some Aliphatic Nitro-compounds.*

By R. N. Haszeldine.

Infra-red spectra of the compounds $R{\cdot}NO_2$ [R = Me, Et, $Pr^n$, $Pr^i$, $Bu^n$, $n$-$C_5H_{11}$, $n$-$C_6H_{13}$, $MeO{\cdot}CH_2{\cdot}CH_2$, CHEtCl, $CMe_2Cl$, $CH_2{\cdot}CO_2Et$, $CBr_3$, $CCl_3$, $CClF_2{\cdot}CF_2$, or $C(NO_2)_3$] have been recorded. The marked influence of R on the asymmetric and symmetric stretching vibrations of the $NO_2$ group, and on the C–N stretching vibration, is discussed.

The nitro-compounds show characteristic absorption in the ultra-violet region, at *ca.* 280 mμ, and only slight shifts occur on replacement of α-hydrogen by chlorine or fluorine. Bromopicrin shows no maximum in this region, and steric effects are postulated. Nitroalkanes, alkyl nitrites, and alkyl nitrates are readily distinguished by their ultra-violet spectra.

The ultra-violet and infra-red spectra of a series of unsubstituted and halogeno-nitroalkanes have been recorded in connection with studies on fluoro-nitro-compounds described in another series (Haszeldine, *J.*, 1953, 2075).

Table 1 records the infra-red spectra of the compounds studied. The assignments made for the asymmetrical stretching (st.-a.) and symmetrical stretching (st.-s.) vibrations of the $NO_2$ group and for the C–N stretching vibration are shown, with other bands in these regions of the spectrum. The Raman spectra of liquid nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane have been recorded by Smith, Pan, and Nielsen (*J. Chem. Phys.*, 1950, **18**, 706), and the Raman spectra of a series of nitro-compounds have been reported by Wittek (*Z. physikal. Chem.*, 1942, *B*, **51**, 103, 187), and the relevant data from these papers have been included in Table 1 for comparison.

The unsubstituted nitroalkanes (and methyl 2-nitroethyl ether) of Table 1 (a) show a very characteristic st.-a. vibration near 1550 $cm.^{-1}$ which changes in position only slightly with change in R. The st.-s. vibration lies in the 1430—1330-$cm.^{-1}$ region which contains other bands arising from the C–H vibrations, but consideration of the infra-red and Raman spectra shows that the st.-s. band falls within the narrow range 1380—1360 $cm.^{-1}$. The C–N stretching vibration appears as a strong band in the spectra of the simpler molecules, and although it becomes more difficult to distinguish from the skeletal vibration in the more complex molecules, a definite assignment can be made.

Table 1 (b) shows the effect of an electron-attracting group (Cl or $CO_2Et$) substituted on the α-carbon atom. The st.-a. band moves to higher frequency, whereas the st.-s. band moves to lower frequency; there is no significant change in the C–N stretching vibration.

Table 1 (c) shows that when the nitro-group is attached to a powerful electron-attracting group, there is a further shift of the st.-a. and st.-s. vibrations to higher and lower frequency, respectively. The C–N assignments are tentative in view of multiple structure in the 920—850-$cm.^{-1}$ region. The shifts to higher frequency of the st.-a. band are correlated with the increased inductive effect of the group R, an effect noted earlier with C:O stretching vibrations (Haszeldine, *Nature*, 1951, **168**, 1028).

The ultra-violet spectra of certain nitro-compounds are shown in Table 2. Earlier work on the ultra-violet spectra of nitro-compounds indicated that they gave a band near 270 mμ (Zelinsky and Rosanoff, *Z. physikal. Chem.*, 1912, **78**, 629; Kortum, *ibid.*, 1939, *B*, **43**, 271; Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 504). The present study has shown that unsubstituted nitroalkanes (and methyl 2-nitroethyl ether) are characterised by a band of low intensity near 280 mμ, whose position moves only slightly with increase in molecular weight of R in $R{\cdot}NO_2$. No difference in spectrum can be detected between primary and secondary unsubstituted nitro-compounds. The usual slight shift to the red is observed on changing the solvent from ethanol to light petroleum, and the spectra of the vapours show that solvent effects are small.

Table 2 also shows that a small but distinct bathochromic effect is obtained on replacement of an α-hydrogen atom by the auxochrome chlorine; the effect of solvent is again

* Part III, *J.*, 1953, 1764.

TABLE 1. *Infra-red and Raman spectra (bands in cm.$^{-1}$) of compounds* $R{\cdot}NO_2$.

| R | | $NO_2$ st.-a. | $NO_2$ st.-s. | C–N st. | Other bands 1650—1250 | Other bands 920—850 |
|---|---|---|---|---|---|---|
| *Section* (a). | | | | | | |
| Me | I.R. | 1567 (vs) | 1379 (s) | 917 (s) | 1422 (m), 1404 (s), 1311 (w) | — |
| | Raman | 1563 | 1376 | 918 | — | — |
| Et | I.R. | 1550 (vs) | 1368 (vs) | 874 (s) | 1460 (s), 1439 (s), 1395 (vs), 1330 (m), 1255 (m) | — |
| | Raman | 1555 | 1366 | 875 | — | — |
| $Pr^n$ | I.R. | 1553 (vs) | 1385 (vs) | 870 (m) or 799 (s) | 1460 (s), 1437 (s), 1344 (m), 1290 (w), 1267 (w) | 897 (m) |
| | Raman | 1555 | 1383 | 872 | — | — |
| $Pr^i$ | I.R. | 1553 (vs) | 1361 (vs) | 851 (s) | 1471 (s), 1399 (vs), 1374 (m), 1304 (m) | 901 (m) |
| | Raman | 1555 | 1357 | 851 | — | — |
| $Bu^n$ | I.R. | 1550 (vs) | 1381 (vs) | 857 (s) | 1466 (s), 1435 (s), 1300 (w), 1277 (w) | 912 (m) |
| | Raman | 1558 | 1383 | — | — | — |
| $n$-$C_5H_{11}$ | I.R. | 1550 (vs) | 1381 (vs) | 876 (s) | 1464 (s), 1437 (s), 1277 (m) | — |
| | Raman | 1550 | 1379 | — | — | — |
| $CHMe_2{\cdot}CH_2$ | I.R. | — | — | — | — | — |
| | Raman | 1550 | 1389 | — | — | — |
| CHMeEt | I.R. | — | — | — | — | — |
| | Raman | 1553 | 1355 | — | — | — |
| $n$-$C_6H_{13}$ | I.R. | 1550 (vs) | 1381 (vs) | 836 (s) | 1464 (s), 1437 (s), 1276 (w) | 893 (m), 870 (m) |
| | Raman | — | — | — | — | — |
| $MeO{\cdot}CH_2{\cdot}CH_2$ | I.R. | 1565 (vs) | 1370 (vs) | 876 (s) or 848 (s) | 1460 (s), 1422 (s), 1395 (s) | — |
| | Raman | — | — | — | — | — |
| *Section* (b). | | | | | | |
| CHEtCl | I.R. | 1570 (vs) | 1340 (s) | 848 (s) | 1460 (s), 1435 (s), 1374 (s), 1299 (m) | 877 (m) |
| $CMe_2Cl$ | I.R. | 1565 (vs) | 1340 (vs) | 850 (s) | 1456 (s), 1395 (s), 1376 (s) | — |
| $CH_2{\cdot}CO_2Et$ | I.R. | 1570 (vs) | 1337 (s) | 859 (s) | 1471 (w), 1449 (w), 1372 (s) | — |
| *Section* (c). | | | | | | |
| $CBr_3$ * | I.R. | 1592 (vs) | 1305 (vs) | 838 (m) | 1397 (w) | 807, 796 (s. doublet) |
| | Raman | 1592 | 1305 | 840 | — | — |
| $CCl_3$ * | I.R. | 1610 (vs) | 1307 (vs) | 842 (m) | 1350 (m), 1277 (w) | 895 (s), 858 (s) |
| | Raman | 1605 | 1307 | 841 | — | — |
| $CClF_2{\cdot}CF_2$ [1] | I.R. | 1618 (vs) | 1274 (vs) | 909 (s) | 1416 (w), 1350 (s) | 821, 816 (s. doublet) |
| $C(NO_2)_3$ | I.R. | 1618 (vs) | 1266 (vs) | — | 1645 (m), 1439 (w), 1370 (m) | 990 (w), 973 (m) |

m = medium, s = strong, vs = very strong, w = weak, s. doublet = strong doublet.

[1] Vapour spectrum.

* Copies of these spectra may be obtained from the Chemical Society ($Br_3C{\cdot}NO_2$, C.S. 47; $Cl_3C{\cdot}NO_2$, C.S. 48).

small. It shows too that further introduction of chlorine on the α-carbon atom causes a shift of the maximum to shorter wave-length. This cannot be attributed to chlorine acting as an auxochrome, since a further shift to the red would have been observed (see Part III, *loc. cit.*), or to the increased inductive effect of the $CCl_3$ group relatively to the CCl group, since the fluorine compound, with the strongly electronegative $CF_2$ group adjacent to the nitro-group, shows a maximum at 282·5 mμ, and fluorine is a less effective auxochrome than chlorine. It is suggested, therefore, that in chloropicrin there is slight steric inhibition of resonance in the nitro-group. This is supported by the complete absence of a maximum or an inflection in the absorption spectrum of bromopicrin in the 240—450-mμ region. Bromine is a better auxochrome than chlorine, and if anything a shift to the red would have been expected. The spectrum of bromopicrin is, in effect, that of the $CBr_3$ part of the molecule ($CBr_4$ has $\varepsilon_{280}$ 290). This suggests steric inhibition of resonance in the $NO_2$ group with distortion of the ONO and/or ONC angles from their usual values. It is noteworthy that steric hindrance to coplanarity of the oxygen atoms with carbon and nitrogen in structures such as (I), with consequent reduction in intensity

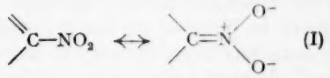
of absorption, has been noted in aromatic nitro-compounds containing alkyl groups *ortho* to the nitro-group (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838).

The nitroalkanes are more readily distinguished from the isomeric nitrites by their ultra-violet spectra than by their infra-red spectra. Butyl and amyl nitrite, for example, show strong absorption at 220 mμ and multiple weak absorption bands in the 320—380-mμ region (Table 2; cf. nitrohexane, nitrobutane). Aliphatic nitrates show only an inflection at *ca.* 260 mμ (Table 2; see also Braude, *Ann. Reports*, 1945, for references to earlier work on nitrites and nitrates).

TABLE 2. *Ultra-violet spectra (light petroleum solution).*

| | $\lambda_{max.}$ | $\varepsilon_{max.}$ | $\lambda_{min.}$ | $\varepsilon_{min.}$ |
|---|---|---|---|---|
| $MeNO_2$ | 278 | 20 | 245 | 7 |
| | 275 [1] | 9 | — | — |
| $EtNO_2$ | 278·5 | 20 | 245·5 | 6 |
| $Pr^nNO_2$ | 280 | 23 | 247 | 10 |
| $Pr^iNO_2$ | 280 | 22 | 245·5 | 5·5 |
| $Bu^nNO_2$ | 279 | 22 | 250 | 12 |
| | 277 [2] | 25 | 248 | 15 |
| $n$-$C_6H_{13}$·$NO_2$ | 279 | 26 | 246 | 9 |
| $MeO·CH_2·CH_2·NO_2$ | 277·5 | 23 | 245·5 | 7 |
| $n$-$C_5H_{11}O·NO$ | 384 | 21 | 382 | 20 |
| | 370 | 45 | 364·5 | 31 |
| | 356·5 | 56 | 349·5 | 30 |
| | 344 | 50 | 338 | 24 |
| | 333 | 37 | 327 | 19 |
| | 323 | 25 | 318·5 | 17 |
| | 313·5 | 20 | 311 | 19 |
| | 218·5 | 1120 | — | — |
| $CHEtCl·NO_2$ | 283·5 | 28 | 249 | 13·5 |
| | 280·5 [2] | 30 | 251 | 17 |
| $CMe_2Cl·NO_2$ | 283·5 | 28 | 248·5 | 8 |
| | 282·5 [2] | 29 | 251 | 11 |
| $CCl_3·NO_2$ | 278·5 | 52 | 247·5 | 16 |
| | 276·5 [2] | 62 | 255·5 | 45 |
| | 277 [1] | 18 | 245 | 7 |
| $CClF_2·CF_2·NO_2$ | 282·5 [1] | 48 | 236·5 | 6 |
| $CBr_3·NO_2$ | General absorption: $\varepsilon_{300}$, 85; $\varepsilon_{280}$, 400; $\varepsilon_{260}$, 1000; $\varepsilon_{240}$, 1800. | | | |
| $C(NO_2)_4$ | General absorption | | | |
| BuO·NO | 384·5 | 33 | 381·5 | 31 |
| | 370 | 70 | 364 | 49 |
| | 356 | 87 | 349 | 46 |
| | 344 | 77 | 337·5 | 36 |
| | 333 | 56 | 326·5 | 27 |
| | 323 | 37 | 318 | 23 |
| | 314 | 27 | 310·5 | 24 |
| | 222 | 1700 | — | — |
| $EtO·NO_2$ | Inflection 255—260 mμ; ε, 17. | | | |

[1] Spectrum of vapour.
[2] Ethanolic solution.



(I)

A combination of ultra-violet and infra-red spectra can thus throw much light on to the structures of unknown nitrogen-containing compounds.

## EXPERIMENTAL

*Compounds.*—Dr. A. I. Vogel, who kindly supplied specimens of many of the compounds shown in Table 1, has reported their physical properties elsewhere. Bromo- and chloro-picrin were obtained from Messrs. Kodak. The 1-chlorotetrafluoro-2-nitroethane was prepared as described in *J.*, 1953, 2075. All specimens were redistilled immediately before use.

*Apparatus.*—The infra-red spectra were recorded on a Perkin–Elmer Model 21 instrument with rock-salt optics. The vapour spectrum was recorded, a 10-cm. gas cell with sodium chloride windows being used.

The ultra-violet spectra were determined on a Unicam Spectrophotometer, using 1- or 10-cm. silica cells. The light petroleum used as solvent had b. p. 60—80°, and was purified by treatment with fuming sulphuric acid. Ethanol (95%) was dried over calcium oxide and distilled in an atmosphere of nitrogen.

*Results.*—The infra-red spectra of the first four compounds of Table 1 were substantially the same as those recorded by Smith *et al.* (*loc. cit*).

In addition to the bands recorded in Table 1 (c), bromopicrin showed absorption at 2899 cm.$^{-1}$ (very weak) and 664 cm.$^{-1}$, and chloropicrin showed bands at 733 (weak), 707 (medium), and 669 cm.$^{-1}$ (medium).

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## 516. *A New Trisaccharide produced from Sucrose by Mould Invertase.*

By J. S. D. Bacon and D. J. Bell.

A non-reducing trisaccharide has been isolated from the products of action of "Takadiastase" (a commercial mould-enzyme preparation) on sucrose. By methylation and analysis of the methylated sugars formed on hydrolysis the following structure has been adduced: *O*-α-D-glucopyranosyl-(1 → 2)-*O*-β-D-fructofuranosyl-(1 → 2) β-D-fructofuranoside. It appears to be formed by enzymic transfer of a β-fructofuranosyl radical to sucrose.

It was found by Edelman (Thesis, Sheffield, 1950), and confirmed by Bealing and Bacon (*Biochem. J.*, 1951, **49**, lxxv), that "Takadiastase," a commercial enzyme preparation probably made from *Aspergillus oryzae*, produces a series of oligosaccharides from sucrose. This action has been found with extracts of all other moulds examined (Wallenfels and Bernt, *Angew. Chem.*, 1952, **64**, 28; Bealing and Bacon, *Biochem. J.*, 1953, **53**, 277), and Pazur (*J. Biol. Chem.*, 1952, **199**, 217) described the partial purification from extracts of *A. oryzae* of a "transfructosidase," which is probably the enzyme responsible. Bealing (*Biochem. J.*, 1953, **55**, 77; Thesis, Sheffield, 1952) put forward the view that this enzyme is, in fact, that hitherto described as "mould invertase," or "glucosaccharase," and that it acts by transferring β-fructofuranosyl radicals from sucrose either to suitable organic acceptors such as sucrose itself, or to water.

Pazur (*loc. cit.*) from a study of $R_F$ values of partial hydrolysis products of inulin has designated as "1-inulobiosyl-D-glucose" a trisaccharide fraction ($[\alpha]_D$ +17° in $H_2O$) isolated by "large-scale filter paper chromatography" from the products of action of his transfructosidase on sucrose.

An adaptation of the chromatographic method of Whistler and Durso (*J. Amer. Chem. Soc.*, 1950, **72**, 677) suggested to one of us (J. S. D. B.) by Dr. A. J. P. Martin, F.R.S., of the National Institute for Medical Research, Mill Hill, revealed that the trisaccharide fraction formed from sucrose by "Takadiastase" consists of at least two components. One of these has been isolated in quantities sufficient for a structural study by methylation.

The essential feature of the modified chromatographic procedure is development by a continuously changing solvent in place of elution by stepwise increase in ethanol concentration. A similar procedure has been developed independently by Alm, Williams, and Tiselius (*Acta Chem. Scand.*, 1952, **6**, 826) and named by them "gradient elution."

The application of the modified technique has shown that components "α" and "β" (cf. Bealing and Bacon, 1953, *loc. cit.*) each consist of at least two substances; these have been designated, in the order in which they emerge from the column, "$\alpha_1$", "$\beta_1$", "$\alpha_2$", and "$\beta_2$". In each case the major component emerges first. The trisaccharide referred to in this paper is "$\alpha_1$", the only one of these substances readily obtained in the pure state. It was not crystallised, but was homogeneous by paper chromatography, as well as by the technique of its isolation. The yields of partially methylated sugars derived from it further suggest homogeneity.

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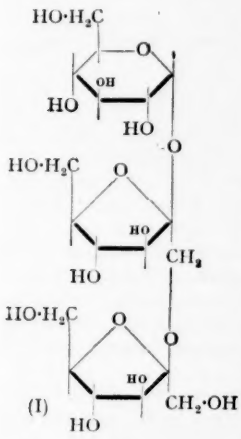
The syrup was four times methylated by the procedure described for kestose [*O*-α-D-glucopyranosyl-(1→2)-*O*-β-D-fructofuranosyl-(6→2) β-D-fructofuranoside] (Albon *et al.*, *loc. cit.*), to give a final yield of 59% of undeca-*O*-methyl-trisaccharide. This on hydrolysis gave 1 : 3 : 4 : 6-tetra-*O*-methyl-D-fructose, 2 : 3 : 4 : 6-tetra-*O*-methyl-D-glucose, and 3 : 4 : 6-tri-*O*-methyl-D-fructose in equimolar proportions. From the ease of hydrolysis by dilute acid, and by yeast invertase preparations free from α-glucosidase, the glucose radical was assumed to be combined as in sucrose. After the substance had been hydrolysed slowly by acetic acid at 40° paper chromatography showed that fructose was liberated more rapidly than glucose, and a non-reducing substance having the $R_F$ value of sucrose was produced. The whole disaccharide fraction from this partial hydrolysate had an $[\alpha]_D$, calculated from its ketose content, consistent with the assumption that it contained only sucrose, and yielded crystalline sucrose from aqueous-ethanol solution.




The tentative structure assigned to the trisaccharide is therefore *O*-α-D-glucopyranosyl-(1→2)-*O*-β-D-fructofuranosyl-(1→2) β-D-fructofuranoside (I), the β-linking being deduced ultimately from the accepted specificity of yeast invertase (cf. Adams, Richtmyer, and Hudson, *J. Amer. Chem. Soc.*, 1943, **65**, 136).

Our methylation studies therefore confirm the ideas of Pazur (*loc. cit.*), and further suggest that the trisaccharide is identical with that present in the artichoke tuber (cf. Bacon and Edelman, *Biochem. J.*, 1951, **48**, 114; Dedonder, *Bull. Soc. Chim. biol.*, 1952, **34**, 144). However, the $[\alpha]_D$ of our substance is higher than that recorded by other authors: Pazur (*loc. cit.*) gives +17° for his trisaccharide, and Dedonder (*loc. cit.*) +23° for "glucofructosane B" from the artichoke. A single preparation of the latter substance by the gradient-elution technique had $[\alpha]_D$ +28°; the artichoke extract apparently contains only a single trisaccharide. The lower value given by Dedonder could be due to some impurity in his preparation, but the much lower figure given by Pazur may be due to the presence of "$\alpha_2$", the $[\alpha]_D$ of which is not known, or possibly of a reducing trisaccharide formed entirely of fructose, that might arise by transfructosidation to free fructose.

The mould trisaccharide described here, like kestose (Albon *et al.*, *loc. cit.*), presumably arises by fructosyl transfer to sucrose. A satisfactory assessment of the differences in specificity between the mould enzyme and yeast invertase must await the characterisation of components I, II, and V of the yeast-invertase reaction mixture (cf. White and Secor, *Arch. Biochem. Biophys.*, 1952, **36**, 490).

## Experimental

Specific rotations were determined in water, in a 2-dm. tube unless otherwise noted.

*Action of "Takadiastase" on Sucrose.*—A solution made by dissolving "Takadiastase" (Parke Davis & Co.) (5·5 g.) in water (25 ml.) was dialysed in Visking synthetic cellulose casing (John Crampton & Co. Ltd., Wythenshawe, Manchester) against running tap-water for 2 days, 5 ml. of toluene being added as a preservative. The dialysed solution was allowed to act on sucrose (20 g.) dissolved in water (80 ml.) and 0·2M-phosphate buffer (pH 7·0) (2 ml.) at room temperature for 20 hr. The enzyme was then inactivated by boiling and the solution stored at −20°. The preparation used for methylation was isolated from this solution. Other reaction mixtures were prepared and yielded essentially similar trisaccharide fractions.

*Chromatography.*—This was based on Whistler and Durso's method (*loc. cit.*). Activated charcoal (British Drug Houses Ltd.) and active carbon No. 130 (Sutcliffe, Speakman & Co. Ltd., Leigh, Lancs.) were used with "Celite No. 535" (Johns Manville Co. Ltd., London, S.W.1.). The charcoals were similar in their properties; the former preparation appeared to have a higher resolving power for sugar mixtures, but the latter was preferred because it gave a neutral effluent.

A typical preparation was as follows: a mixture of active carbon No. 130 (40 g.) and "Celite No. 535" (40 g.) was packed wet (350 ml. of water) into a glass tube, forming a column 28 mm. in diam. and about 400 mm. high. The enzyme reaction mixture (10 ml.) was allowed

## 516. *A New Trisaccharide produced from Sucrose by Mould Invertase.*

By J. S. D. Bacon and D. J. Bell.

A non-reducing trisaccharide has been isolated from the products of action of "Takadiastase" (a commercial mould-enzyme preparation) on sucrose. By methylation and analysis of the methylated sugars formed on hydrolysis the following structure has been adduced: *O*-α-D-glucopyranosyl-(1 → 2)-*O*-β-D-fructofuranosyl-(1 → 2) β-D-fructofuranoside. It appears to be formed by enzymic transfer of a β-fructofuranosyl radical to sucrose.

It was found by Edelman (Thesis, Sheffield, 1950), and confirmed by Bealing and Bacon (*Biochem. J.*, 1951, **49**, lxxv), that "Takadiastase," a commercial enzyme preparation probably made from *Aspergillus oryzae*, produces a series of oligosaccharides from sucrose. This action has been found with extracts of all other moulds examined (Wallenfels and Bernt, *Angew. Chem.*, 1952, **64**, 28; Bealing and Bacon, *Biochem. J.*, 1953, **53**, 277), and Pazur (*J. Biol. Chem.*, 1952, **199**, 217) described the partial purification from extracts of *A. oryzae* of a "transfructosidase," which is probably the enzyme responsible. Bealing (*Biochem. J.*, 1953, **55**, 77; Thesis, Sheffield, 1952) put forward the view that this enzyme is, in fact, that hitherto described as "mould invertase," or "glucosaccharase," and that it acts by transferring β-fructofuranosyl radicals from sucrose either to suitable organic acceptors such as sucrose itself, or to water.

Pazur (*loc. cit.*) from a study of $R_F$ values of partial hydrolysis products of inulin has designated as "1-inulobiosyl-D-glucose" a trisaccharide fraction ($[\alpha]_D$ +17° in $H_2O$) isolated by "large-scale filter paper chromatography" from the products of action of his transfructosidase on sucrose.

An adaptation of the chromatographic method of Whistler and Durso (*J. Amer. Chem. Soc.*, 1950, **72**, 677) suggested to one of us (J. S. D. B.) by Dr. A. J. P. Martin, F.R.S., of the National Institute for Medical Research, Mill Hill, revealed that the trisaccharide fraction formed from sucrose by "Takadiastase" consists of at least two components. One of these has been isolated in quantities sufficient for a structural study by methylation.

The essential feature of the modified chromatographic procedure is development by a continuously changing solvent in place of elution by stepwise increase in ethanol concentration. A similar procedure has been developed independently by Alm, Williams, and Tiselius (*Acta Chem. Scand.*, 1952, **6**, 826) and named by them "gradient elution."

The application of the modified technique has shown that components "α" and "β" (cf. Bealing and Bacon, 1953, *loc. cit.*) each consist of at least two substances; these have been designated, in the order in which they emerge from the column, "$\alpha_1$", "$\beta_1$", "$\alpha_2$", and "$\beta_2$". In each case the major component emerges first. The trisaccharide referred to in this paper is "$\alpha_1$", the only one of these substances readily obtained in the pure state. It was not crystallised, but was homogeneous by paper chromatography, as well as by the technique of its isolation. The yields of partially methylated sugars derived from it further suggest homogeneity.

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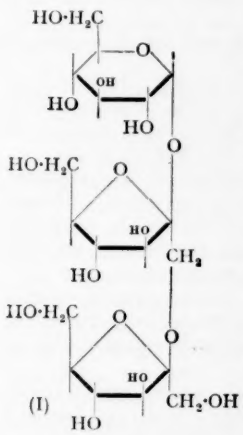


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to soak into the top of the column and was washed in with water (15 ml.). The top of the column was then attached through a narrow siphon tube to a closed 1-l. conical flask full of water (1000 ml.), into which 50% aqueous ethanol (v/v) was allowed to drip to replace the fluid which entered the charcoal–Celite column; the contents of the flask were stirred by a magnetic stirrer operating for 1 min. in each 5-min. period (cf. Alm *et al.*, *loc. cit.*). In this way the concentration of ethanol in the solvent entering the column increased in a reproducible manner. Monosaccharide, mainly glucose, emerged after 250 ml. of effluent had passed, disaccharide, mainly sucrose, after 440 ml., and "$\alpha_1$" after 560 ml.; the sucrose and trisaccharide fractions overlapped to a slight extent, "$\alpha_1$" and "$\beta_1$" to a somewhat greater extent, but the greater part of "$\alpha_1$" was apparently homogeneous. The concentrations of sugars in the effluent were such that 5 μl. contained an ample amount for examination by paper chromatography. By two such operations about 900 mg. were obtained for methylation.

The optical rotation of such fractions was read in 2—5% solution, and the same solution analysed by the methods described by Bacon and Edelman (*loc. cit.*).

The material was converted into a mixture of glucose and fructose by the action of yeast invertase (B.D.H. "Invertase Concentrate") or of dilute acid. No intermediates were detected in enzymic hydrolyses, but on addition of acetic acid (20% by vol.) at 40° appreciable amounts of a non-reducing disaccharide were formed. After hydrolysis for 6 hr. in this manner 68 mg. of a disaccharide fraction were isolated by the gradient-elution technique from 0·5 g. of trisaccharide. 48 Mg. of the fraction (ketose content, 22·5 mg.) in 3 ml. of water had a rotation of +1·88°; on the assumption that it is sucrose the rotation corresponds to $[\alpha]_D$ +66° (sucrose has $[\alpha]_D$ +66·5°). The fraction was dissolved in 75% aqueous ethanol (3 ml.) and treated with charcoal (30 mg.). The filtrate was taken to dryness and dissolved in 50% aqueous ethanol (0·25 ml.). Absolute ethanol (2 ml.) was added and the solution set aside. There was a growth of crystals, m. p. 186° (mixed m. p. with authentic sucrose, 184—185°); 5·6 mg. treated with 1·2 mg. of diazouracil in 0·5 ml. of N-sodium hydroxide at 10° gave the deep blue-green colour typical of sucrose.

Tests were carried out as described by Raybin (*loc. cit.*) on 50-mg. samples of the trisaccharide, and also on 10-mg. samples with one-fifth quantities of reagents. In no case was any green colour observed. Sucrose and raffinose gave typical blue-green colours, and melezitose and kestose a brownish-yellow colour, similar to that given by the mould trisaccharide.

*Methylation of the Trisaccharide.*—880 Mg. were treated as described for kestose (Albon *et al.*, *loc. cit.*); 680 mg. (59%) of *undeca*-O-*methyl-trisaccharide* were obtained (average loss per methylation ~10%) as a syrup having $n_D^{20}$ 1·4613 (decrement for rise in temp. of 1°, 0·00034) and $[\alpha]_D^{20}$ +27·9° (*c*, 2·5) (Found: C, 53·4; H, 8·4; OMe, 51·2. $C_{30}H_{54}O_{16}$ requires C, 53·2; H, 8·05; OMe, 51·8%).

*Hydrolysis Products of the Methylated Trisaccharide* (cf. Albon *et al.*, *loc. cit.*).—320 Mg. were heated in 0·05N-sulphuric acid (25 ml.) at 100° till a constant $[\alpha]_D^{20}$ of +44·6° was observed (*l*, 4). This rotation corresponds closely to that expected from an equimolar mixture of 1 : 3 : 4 : 6-tetra-*O*-methyl-D-fructose, 2 : 3 : 4 : 6-tetra-*O*-methyl-D-glucose, and 3 : 4 : 6-tri-*O*-methyl-D-fructose (cf. Bell, *J.*, 1953, 1231). Paper chromatography showed the presence of both of the first two sugars along with that of a tri-*O*-methylketose moving at the same rate as the above-mentioned fructose derivative.

Silica column chromatography of the mixed hydrolysis products (320 mg.) gave two clear-cut fractions. The toluene eluate (190 mg.) had $[\alpha]_D^{20}$ +56·7° (calc., +55·9°); further examination by the procedure previously used with methylated kestose gave crystalline 2 : 3 : 4 : 6-tetra-*O*-methyl-D-glucose (m. p. and mixed m. p. 95—98°) and a syrup having the chromatographic properties of 1 : 3 : 4 : 6-tetra-*O*-methylfructose. The methanolic eluate of the column yielded 99 mg. (97%) of a syrup (OMe, 41·2%), $[\alpha]_D^{20}$ +29·3°, $n_D^{20}$ 1·4652. This was proved to be 3 : 4 : 6-tri-*O*-methyl-D-fructose, since (*a*) 24·63 mg. oxidised by $IO_4^-$ (Bell, Palmer, and Johns, *J.*, 1949, 1536; Bell and Palmer, *J.*, 1952, 3763) gave 31·93 mg. (0·97 mol.) of formaldehyde–dimedone compound, m. p. 190—192° (corr.) and (*b*) the sugar yielded 3 : 4 : 6-tri-*O*-methyl-D-glucose phenylosazone, m. p. and mixed m. p. 125—126°.

This work was done with the technical assistance of Miss B. Dickinson. We thank Dr. Martin for his suggestion about the chromatographic procedure, and Miss J. Cawkwell for assistance during the early stages.

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THE UNIVERSITIES OF SHEFFIELD AND CAMBRIDGE. [*Received, April 17th*, 1953.]

# 517. *Cyanamides. Part VI.* Sulphonyl Derivatives related to Dicyandiamide and Melamine.*

By Frederick Kurzer and J. Roy Powell.

*N*-Aryl(or -alkyl)sulphonyl-*N'*-cyanoguanidines are converted into *N*-(sulphonylamidino)ureas, *N*-(sulphonylamidino)thioureas, and *N*-sulphonyldiguanides, by hydrolysis, addition of hydrogen sulphide, and ammonolysis, respectively. They react with sulphonyl halides in pyridine to yield trisulphonylmelamines, the structures of which are established by degradation.

In continuation of work on the interaction of sulphonyl halides with compounds incorporating the urea structure (Kurzer, *Chem. Reviews*, 1952, **50**, 1), the behaviour of 1-arylbiurets in this reaction has been examined (Kurzer and Powell, *Chem. and Ind.*, 1953, 195). The observed production of polymeric forms of sulphonylcyanamides necessitated a closer examination of sulphonyl derivatives of dicyandiamide and related compounds.

The introduction of two sulphonyl groups into dicyandiamide appeared to be a possible route to dimeric sulphonylcyanamides. Monosulphonyl derivatives of dicyandiamide, and their hydrolytic conversion into sulphonylamidinoureas, have been described by Kaiser and Thurston (U.S.P. 2,368,841; 2,426,882; B.P. 566,864). The results of their parallel work on carbonyldicyandiamides (*J. Org. Chem.*, 1952, **17**, 185, 1162) and the observations now presented suggest that sulphonyldicyandiamides may be regarded as *N*-cyano-*N'*-sulphonylguanidines (I).

By Kaiser and Thurston's method, a number of *N*-cyano-*N'*-sulphonylguanidines (I) were prepared in fair yields from dicyandiamide and sulphonyl chlorides in alkaline media containing a suitable organic solvent, *e.g.*, acetone; the presence of the latter proved essential since interaction in purely aqueous alkalis afforded only negligible yields of (I), the bulk of the dicyandiamide being recovered as amidinourea arylsulphonate. The products (I), though rapidly and quantitatively hydrolysed to the sulphonylamidinoureas (III) by dilute hydrochloric acid, or more slowly by mixtures of water and organic solvents (Kaiser and Thurston, *loc. cit.*), were sufficiently unaffected by boiling water to be readily recrystallised therefrom; they were quite stable towards alkalis.

The results of the addition of hydrogen sulphide and ammonia, respectively, to the products (I) thus obtained confirmed the presence of a cyanamide grouping. Hydrogen sulphide and *N*-cyano-*N'*-sulphonylguanidines, in pyridine–triethylamine (cf. Fairfull, Low, and Peak, *J.*, 1952, 742) gave good yields of *N*-(sulphonylamidino)thioureas (IV), reconvertible into the starting materials (I) by lead acetate in alkali. *N*-Arylsulphonyl-*N'*-cyanoguanidines (I) reacted with aqueous ammonia on prolonged treatment under pressure at 110°, in the presence of copper sulphate, to give small yields (7—12%) of the characteristic pink copper complexes of diguanides from which the free arylsulphonyldiguanides (V) were readily isolated; much of the starting material (30—40%) remained unchanged, however, and part of it was consumed in a side reaction, being hydrolysed to the corresponding arylsulphonylguanidine (12—32%). Depending on the particular reactants selected, the rates of conversion of dicyandiamides into diguanides are known to lie between wide limits (cf. Curd and Rose, *J.*, 1946, 729). In the present case, the low rate of condensation of the substituted dicyandiamide with ammonia and the loss of starting material in the simultaneous hydrolysis undoubtedly combined to lower the yields, which could, therefore, not be greatly improved by prolonging the time of reaction. *N*-Arylsulphonyldiguanides (V) thus obtained were identical with specimens prepared from arylsulphonyl halides and diguanide by the procedure described for the synthesis of sulphanilyldiguanide (Rose, B.P. 550,538). Since, in the latter reaction, the sulphonyl halide may be assumed to attack a terminal nitrogen of the diguanide molecule, the arylsulphonyldiguanides obtained by both routes may be regarded as (V). This evidence rules out the alternative structures (II) for the original sulphonyldicyandiamides. Their solubility in aqueous alkalis and non-solubility in acids are in agreement with this view.

* Part V, *J.*, 1951, 1258.

Although acyldicyandiamides are readily convertible into the corresponding acylbiurets by hydrolysis in a variety of acid media (Adams, U.S.P. 2,401,599), attempts to obtain arylsulphonylbiurets (VI) from *N*-cyano-*N'*-sulphonylguanidines were unsuccessful. With moderately concentrated aqueous-ethanolic sulphuric acid, the reaction proceeded only to the amidinourea stage; under more vigorous conditions the molecule was ruptured, arylsulphonamide being formed as one of the main products.

$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}CN$ (I)

$NH_2{\cdot}C(:NH){\cdot}N(SO_2R){\cdot}CN$ (II)

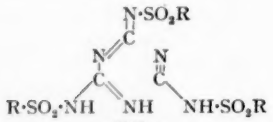
$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}CO{\cdot}NH_2$ (III)

$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}CS{\cdot}NH_2$ (IV)

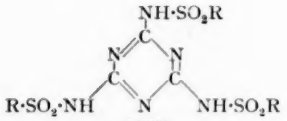
$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}C(:NH){\cdot}NH_2$ (V)

$R{\cdot}SO_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$ (VI)

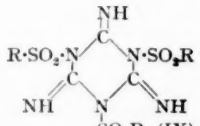
$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}N(SO_2R){\cdot}CN$ (VII)



(VII*a*)



(VIII)



(IX)

The attempted introduction of a second sulphonyl residue into *N*-cyano-*N'*-sulphonylguanidines (I) did not result in formation of disulphonyldicyandiamides. Since sulphonyldicyandiamides (I) are prepared by the use of an excess of sulphonyl halide, it was not unexpected that they failed to react with a second equivalent of sulphonyl chloride in alkalis. Interaction in pyridine at moderate temperatures, however, rapidly afforded good yields of products which were identified as tri-aryl (or -alkyl)sulphonylmelamines. Their suggested structure (VIII) was proved by molecular-weight determinations and hydrolytic degradation. Concentrated sulphuric acid, known as a suitable reagent for splitting the nitrogen–sulphur link of the sulphonamide group (Ciba, Swiss P. 88,561; Kuhn and Reinemund, *Ber.*, 1934, **67**, 1932; Hodgson and Birtwell, *J.*, 1943, 433; Thorp and Walton, *J.*, 1948, 559), afforded melamine and the appropriate sulphonic acid. Prolonged treatment with ethanolic hydrochloric acid gave satisfactory yields of cyanuric acid and the requisite sulphonamide. In the absence of rearrangements, the latter observations exclude the alternative *iso*melamine structure (IX): sulphonamides cannot presumably be formed from sulphonyl*iso*melamines without the disruption of the triazine nucleus. Formula (VIII) derives further support from the observed acidic nature of the compounds; *iso*melamines (IX) may be expected to be predominantly basic (cf. Part III, *J.*, 1949, 3033).

In order to establish that the triazine system had not been formed from a dimeric sulphonylcyanamide during the above hydrolyses, a sulphonyldicyandiamide (I) was subjected to these reactions under identical conditions. In sulphuric acid, *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine decomposed with evolution of carbon dioxide and gave guanidine, isolated as the toluene-*p*-sulphonate. Dicyandiamide itself is known to yield guanidine under similar conditions (Lidholm, *Ber.*, 1913, **46**, 158; Davis, *J. Amer. Chem. Soc.*, 1921, **43**, 670). Ethanolic hydrochloric acid gave a mixture of sulphonylamidinourea (III), sulphonylguanidine, and sulphonamide. The non-formation of triazines during the original degradation experiments appeared therefore to be confirmed.

The production of trisulphonylmelamines (VIII) in the present reaction may be regarded as an extension of the well-known synthesis involving the corresponding parent compounds: melamine is prepared on the industrial scale by heating dicyandiamide, usually in the presence of ammonia as a diluent (for a review, see McClellan, *Ind. Eng. Chem.*, 1940, **32**, 1181), or by heating solutions of this dimer with or without the addition of cyanamide (B.P. 598,533) in anhydrous tertiary bases (B.P. 599,702). As suggested by Davis and Underwood (*J. Amer. Chem. Soc.*, 1922, **44**, 2595), melamine may be regarded as arising by combination of dicyandiamide and cyanamide, which in turn originates from the breakdown of part of the dimer.

The results of experiments on the interaction of *N*-aryl-*N'*-cyanoureas (Kurzer and

Powell, *loc. cit.*), and those of the present investigation suggest that structures incorporating a $\cdot N(SO_2R)\cdot CN$ grouping in proximity to a mobile hydrogen atom are labile and decompose immediately in pyridine solution with elimination of the elements of sulphonylcyanamide ($R\cdot SO_2\cdot NH\cdot CN$). A possible mechanism for the present synthesis of trisulphonylmelamines (VIII) may therefore involve the intermediate formation of *N*-cyano-*NN'*-disulphonylguanidines (VII); their fission into two molecules of sulphonylcyanamides would provide the fragments (*i.e.*, the unchanged dimer, and monomer being formed) from which the triazine is built up. In addition to chemical evidence, *X*-ray analyses (Hughes, *J. Amer. Chem. Soc.*, 1940, **62**, 1258) and measurements of dipole moments (Schneider, *ibid.*, 1950, **72**, 761) have recently led to the suggestion that the dicyandiamide molecule is best represented as a resonance hybrid, to which di-imide structures contribute significantly. Interaction of the carbodi-imide configuration of the dimeric sulphonylcyanamide (VII*a*) and the monomer would lead directly to sulphonylmelamines (VIII).

## Experimental

(The pyridine used was the commercially available anhydrous grade.)

N-*Cyano*-N'-*toluene*-p-*sulphonylguanidine*.—A suspension of dicyandiamide (25·2 g., 0·3 mole) in aqueous potassium hydroxide (14·0 g., 0·25 mole; dissolved in 28 ml. of water) was mechanically stirred at 30° for 10 min., after which acetone (100 ml.) was added. The well-stirred, two-phase system was treated, during 1—1½ hr., with a solution of toluene-*p*-sulphonyl chloride (47·6 g., 0·25 mole) in acetone (80 ml.) at 30—32° (cooling), alkalinity being maintained, towards the end, by simultaneous dropwise addition of more potassium hydroxide solution (20 g., 0·36 mole, in 20 ml. of water). The suspension of the resulting crystalline potassium salt was then stirred at 30—32° for a further ½ hr. and cooled to 0°, and the white solid (52—55 g.) filtered off and washed with a little acetone (recovery of further quantities of this salt from the filtrates by evaporation proved impracticable). The salt was dissolved in water (450—550 ml.) at 80—85°, the liquid quickly filtered while hot, and the filtrate allowed to cool until crystallisation had just set in. Concentrated hydrochloric acid (40 ml.) was then quickly added, and the crystallisation of the free acid completed by slowly cooling the suspension to 0°. The product (m. p. 195—210°, decomp.; 30—32·7 g., 50—55%), crystallised several times from boiling water (150 ml. per g.), affords needles of N-*cyano*-N'-*toluene*-p-*sulphonylguanidine*, m.p. 215—218° (decomp.) (slight sintering at 193°) (recovery per crystallisation: over 85%) (Found: C, 45·4, 45·3; H, 4·25, 4·3; N, 23·8; S, 12·9. $C_9H_{10}O_2N_4S$ requires C, 45·4; H, 4·2; N, 23·5; S, 13·4%). The substance was recovered unchanged after 2 hr.' refluxing in aqueous sodium hydroxide (2% w/v).

The interaction of dicyandiamide (0·05 mole) and toluene-*p*-sulphonyl chloride (0·1 mole) in 10% aqueous sodium hydroxide (0·2 mole) at 20—40° gave a solution which deposited, on acidification at room temperature, *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine, m. p. (193°) 215—217° (decomp.) (2—5%). Partial evaporation of the aqueous acid (Congo-red) filtrate gave amidinourea toluene-*p*-sulphonate (60—80%), m. p. and mixed m. p. 244—246° (decomp.) (Found: N, 20·4; S, 11·8. Calc. for $C_9H_{14}O_4N_4S$: N, 20·4; S, 11·7%).

Addition of *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine (2·38 g., 0·01 mole) to liquid ammonia (30 ml.) and spontaneous evaporation of the clear solution gave its *ammonium* salt (92—96%), which formed flat prisms, m. p. 219—220° (decomp.), when crystallised from water (20 ml. per g.) (Found: C, 42·85; H, 4·8; N, 27·8. $C_9H_{13}O_2N_5S$ requires C, 42·35; H, 5·1; N, 27·45%). The *ammonium* salts of *N*-benzenesulphonyl-*N'*-cyanoguanidine, m. p. 220—223° (decomp.) (from water, 10 ml. per g.) (Found: N, 28·0. $C_8H_{11}O_2N_5S$ requires N, 29·05%), and of *N*-*p*-aminobenzenesulphonyl-*N'*-cyanoguanidine, m. p. 228—229° (decomp.) (from water, 3 ml. per g.) (Found: N, 32·4. $C_8H_{12}O_2N_6S$ requires N, 32·8%), were similarly prepared.

N-*Cyano*-N'-*toluene*-o-*sulphonylguanidine* was similarly prepared, first as potassium salt, which, on dissolution in water (600—650 ml. at 75°, in experiments starting with 0·3 mole of dicyandiamide), precipitation with hydrochloric acid, and cooling, gave the almost pure *compound* (m. p. 170—174°, decomp.) in 20—25% yield. It formed prisms, m. p. 173—174° (decomp.), from boiling ethanol (2—3 ml. per g.) (Found: C, 45·5; H, 4·4. $C_9H_{10}O_2N_4S$ requires C, 45·4; H, 4·2%).

N-*Cyano*-N'-*methanesulphonylguanidine* was prepared by simultaneous addition, during 1½ hr., of a solution of methanesulphonyl chloride (28·6 g., 0·25 mole) in acetone (40 ml.), and

aqueous potassium hydroxide (28 ml., 60% w/v, 0·3 mole), to a stirred suspension of dicyandiamide (16·8 g., 0·2 mole) in aqueous potassium hydroxide (19 ml., 60% w/v, 0·2 mole)–acetone (60 ml.). The temperature was kept below 8° by external ice-cooling. The separated potassium salt was dissolved in water (40 ml.) at 60°; the product was precipitated with hydrochloric acid, filtered off at 0° (12—14 g.; 37—43%), and crystallised from boiling ethanol (50 ml. per g.), giving prisms of the *guanidine*, m. p. 179—180° (decomp.) (Found: C, 22·5; H, 4·0; N, 35·0; S, 19·9. $C_3H_6O_2N_4S$ requires C, 22·2; H, 3·7; N, 34·6; S, 19·75%). The use of excess of dicyandiamide, of less concentrated potassium hydroxide solutions, or temperatures exceeding 8° resulted in much diminished yields.

N-(*Benzenesulphonylamidino*)*thiourea*.—A solution of *N*-benzenesulphonyl-*N'*-cyanoguanidine (2·24 g., 0·01 mole) in a mixture of anhydrous pyridine (10 ml.) and anhydrous triethylamine (1·0 g., 0·01 mole), kept at 40—50°, was slowly treated (12 hr.) with a stream of dry hydrogen sulphide. The deep orange-red liquid was poured into water (20 ml.), freed from colloidal sulphur by filtration with carbon, and acidified (to Congo-red) with dilute hydrochloric acid. The collected precipitate was crystallised four times from ethanol (20 ml. per g.), the solution being each time decanted from traces of undissolved sulphur, and gave lustrous platelets of N-(*benzenesulphonylamidino*)*thiourea*, m. p. 202—203° (decomp.) (Found: C, 36·8; H, 3·8; S, 25·2. $C_8H_{10}O_2N_4S_2$ requires C, 37·2; H, 3·9; S, 24·8%) (yield, including material recovered from the ethanolic filtrates: 1·74 g., 67%). Hydrogen sulphide treatment over shorter periods resulted in incomplete conversion of the reactant.

N-(*Toluene*-p-*sulphonylamidino*)*thiourea*, similarly prepared from *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine, crystallised from ethanol (10 ml. per g.) in needles, m. p. 201—202° (decomp.) (83%) [Found: C, 40·1; H, 4·6; S, 22·8%; *M* (Rast), 300. $C_9H_{12}O_2N_4S_2$ requires C, 39·7; H, 4·4; S, 23·5%; *M*, 272]. N-(p-*Aminobenzenesulphonylamidino*)*thiourea*, similarly prepared (in 76% total yield), formed needles, m. p. 195—197° (decomp.), after two crystallisations from water (30 ml. per g.) and one from ethanol (20 ml. per g.), (Found: C, 35·9; H, 3·8; S, 22·8. Calc. for $C_8H_{11}O_2N_5S_2$: C, 35·2; H, 4·0; S, 23·4%). [This compound was prepared from amidinothiourea and *p*-nitrobenzenesulphonyl chloride, followed by reduction (Winnek, U.S.P. 2,303,972), but the m. p. was not given.]

*Desulphurisation of* N-(*Toluene*-p-*sulphonylamidino*)*thiourea*.—A boiling solution of this thiourea (2·72 g., 0·01 mole) in aqueous potassium hydroxide (56 ml., 5% w/v, 0·05 mole) was treated with a saturated aqueous solution of lead acetate trihydrate (7·6 g., 0·02 mole). The suspension was stirred at 80—60° for 5 min., the lead sulphide filtered off at the pump, and the cooled filtrate acidified to Congo-red. The collected precipitate (1·35 g., 57%) was crystallised from water and gave needles of *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine (m. p. undepressed by authentic material) (Found: C, 44·5; H, 4·1%).

*Toluene*-p-*sulphonyldiguanide*.*—(a) *From diguanide*. A stirred suspension of diguanide sulphate (preparation: Ostrogovich, *Chem. Zentr.*, 1910, II, 1890; isolation as sulphate: Rackmann, *Annalen*, 1910, **376**, 170) (2·20 g., 0·01 mole) in acetone (10 ml.) and aqueous sodium hydroxide (20% w/v; 4 ml., 0·02 mole) was treated, during 15 min. at 3—8°, with a solution of toluene-*p*-sulphonyl chloride (1·90 g., 0·01 mole) in acetone (4 ml.), followed by more aqueous sodium hydroxide (2 ml., 0·01 mole). The separated product (m. p. 238—242°, decomp.; 2·15 g., 85%), collected after a further 15 min.' stirring, was crystallised successively from water (180 ml. per g.) and ethanol (100 ml. per g.) and gave plates of *toluene*-p-*sulphonyldiguanide*, m. p. 246—247° (decomp.) (Found: C, 42·7; H, 5·1; N, 27·1. $C_9H_{13}O_2N_5S$ requires C, 42·35; H, 5·1; N, 27·45%).

(b) *From* N-*cyano*-N'-*toluene*-p-*sulphonylguanidine*. A suspension of this guanidine (2·38 g., 0·01 mole) and powdered copper sulphate pentahydrate (2·50 g., 0·01 mole) in ammonia (8·5% w/v, 40 ml.), contained in a closed vessel, was heated for 18 hr. in a brine-bath (108—110°). The resulting suspension was heated to boiling, the supernatant deep blue liquid decanted (through a funnel), and the remaining solid, after having been once again extracted with boiling water (50 ml.), collected on the same funnel (combined filtrates B). The pink solid (0·65 g.) was extracted with boiling ethanol (2 × 20 ml.), and filtered off (filtrates A). The residual pink copper salt (0·35 g.) was dissolved in warm hydrochloric acid (10%; 8 ml.), the copper removed by precipitation with hydrogen sulphide and filtration, and the crude product precipitated from the filtrate with concentrated aqueous ammonia. Crystallisation from water (30 ml.), followed by extraction of the crystalline solid with boiling ethanol (3 ml.) to remove traces of

* The m. p. given for this compound in the preliminary note (*Chem. and Ind.*, 1953, 195) is incorrectly stated and is in fact the m. p. of the ammonium salt of the corresponding *N*-arylsulphonyl-*N'*-cyanoguanidine.

toluene-*p*-sulphonylguanidine, gave toluene-*p*-sulphonyldiguanide (0·18 g., 7%), m. p. 243—245° (decomp.), mixed m. p. with material prepared by method (a) 241—243° (Found: C, 42·5; H, 5·15; N, 26·9%). Filtrates (A) deposited toluene-*p*-sulphonylguanidine (0·23 g.), m. p. and mixed m. p. 203—204°. The alkaline filtrates (B) were acidified with concentrated hydrochloric acid (Congo-red), and the white crystalline precipitate collected at 0° (1·50 g.). Extraction with aqueous sodium hydroxide (4% w/v, 25 and 10 ml.) left a residue of toluene-*p*-sulphonylguanidine, m. p. 203—204° (from ethanol) (0·20 g., *i.e.*, total yield 20%). Acidification of the alkaline extracts gave unchanged starting material (1·10 g., 45%).

*Benzenesulphonyldiguanide* • was prepared by method (a) in 90% yield; successive crystallisation from water (50 ml. per g.) and ethanol (60 ml. per g.) gave the *diguanide* as platelets, m. p. 232—234° (decomp.) (Found: C, 40·0; H, 4·7; N, 29·7; S, 13·5. $C_8H_{11}O_2N_5S$ requires C, 39·8; H, 4·6; N, 29·05; S, 13·3%). The interaction of *N*-benzenesulphonyl-*N'*-cyanoguanidine and ammonia in the presence of copper sulphate (quantities, conditions, and isolation as above) gave the following products: unchanged starting material (30%); benzenesulphonylguanidine, m. p. and mixed m. p. 210—211° (0·63 g., 32%) [picrate: m. p. and mixed m. p. (Clarke and Gillespie, *J. Amer. Chem. Soc.*, 1932, **54**, 1964) 188—189° (decomp.)]; benzenesulphonyldiguanide, m. p. and mixed m. p. with material prepared by method (a) 231—233° (decomp.) (0·29 g., 12%).

*Toluene*-p-*sulphonylamidinourea*.—To a boiling suspension of *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine (7·14 g., 0·03 mole) in aqueous sulphuric acid (12%, 30 ml.), ethanolic sulphuric acid (12%, 90 ml.) was added, and the resulting solution refluxed for 1 hr. Deposition of solid began after 20—30 min.; the separated material was collected at 0° (m. p. 224—230°; 6·3 g., 82%). Two crystallisations from ethanol (100 ml. per g., 60% recovery per crystn.) gave platelets of the *urea*, m. p. 238—242° (decomp.) (Found: C, 42·1; H, 4·8; N, 21·6. $C_9H_{12}O_3N_4S$ requires C, 42·2; H, 4·7; N, 21·9%). The same material, m. p. and mixed m. p. 239—242° (decomp.), was obtained (60%) by Kaiser and Thurston's procedure (*loc. cit.*), *i.e.*, hydrolysis with boiling 10% hydrochloric acid during 10 min. Prolonged boiling (6 hr.) with 12% or 25% aqueous-ethanolic sulphuric acid gave the above amidinourea (in 35—5% yield) and toluene-*p*-sulphonamide (in 30—60% yield).

*Toluene*-o-*sulphonylamidinourea* was similarly prepared in 78% yield. Two crystallisations from ethanol (80 ml. per g.) gave plates of the *product*, m. p. 228—230° (decomp.) (Found: C, 42·3; H, 4·55; N, 21·2. $C_9H_{12}O_3N_4S$ requires C, 42·2; H, 4·7; N, 21·9%). *Methanesulphonylamidinourea* was similarly prepared (by use of 12% aqueous sulphuric acid only) in 40% yield. Crystallisation from ethanol (150 ml. per g.) gave needles, m. p. 217—219° (decomp.) (Found: C, 19·8; H, 4·15; N, 30·9. $C_3H_8O_3N_4S$ requires C, 20·0; H, 4·4; N, 31·1%).

*Tri(toluene*-p-*sulphonyl)melamine*.—A solution of *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine (7·14 g., 0·03 mole) in anhydrous pyridine (40 ml.) at 25° was treated with toluene-*p*-sulphonyl chloride (8·55 g., 0·045 mole). The clear, orange liquid was kept at 90—95° for ½ hr. and then slowly stirred into a mixture of ice (120 g.), water (120 ml.), and concentrated hydrochloric acid (50 ml.). The white granular solid was filtered off and stirred with aqueous sodium hydroxide (6% w/v; 150 ml.), a small insoluble fraction filtered off (0·5—0·8 g.; m. p. >360°), and the product slowly reprecipitated with hydrochloric acid (1 : 1; 60 ml.). The collected air-dried powder [12—14 g., m. p. 130—150° (sintering at 110—125°, and finally giving a deep orange melt)] was added to boiling ethanol (100 ml.) in which it dissolved almost instantly. The orange solution rapidly deposited crystalline scales which were filtered off at 0° (m. p. 280—282°; 8·8—10·0 g., 75—85%) (ethanolic filtrate A). Crystallisation from boiling ethanol (60 ml. per g., recovery approx. 75% per crystallisation) gave platelets of *tri(toluene*-p-*sulphonyl)melamine*, m. p. 284—285° [Found: C, 48·7; H, 4·6; N, 14·2; S, 15·9%; *M* (Rast), 560, 590. $C_{24}H_{24}O_6N_6S_3$ requires C, 49·0; H, 4·1; N, 14·3; S, 16·3%; *M*, 588]. Filtrates A very slowly deposited more product (m. p. 280—282°). The melamine derivative was readily soluble in pyridine and liquid ammonia, moderately soluble in warm dilute caustic alkalis and boiling acetone, sparingly soluble in boiling benzene, and practically insoluble in ether. When reprecipitated by acids from its solution in dilute aqueous alkali, it formed a white amorphous powder (m. p. 150—175°, resolidifying at 180—190° and finally melting at 270—275°) of greatly increased solubility when added to boiling ethanol (probably owing to hydration). Dissolution in ethanol gave once again platelets, m. p. 285°.

*Tri(toluene*-o-*sulphonyl)melamine*.—*N*-Cyano-*N'*-toluene-*o*-sulphonylguanidine (7·14 g., 0·03 mole) in pyridine (90 ml.) was treated with toluene-*o*-sulphonyl chloride (11·4 g., 0·06 mole) at 30° and kept at 90—95° for 20 min. The crude air-dried reprecipitated product, isolated as

above, was added to boiling ethanol (60 ml.) (or to boiling chloroform, 100 ml.); the clear solution rapidly deposited crystalline prisms on cooling (m. p. 280°; 5·3 g., 45%). The filtrate therefrom was evaporated in a vacuum, the oily residue dissolved in aqueous alkali (12% w/w, 30 ml.) and filtered (carbon), and the product reprecipitated with acid. Dissolution of the air-dried precipitate in ethanol gave a second crop of crystalline material; a third crop was similarly obtained (total, 1·2—1·75 g., 10—15%). Two crystallisations from acetone (150 ml. per g., recovery approx. 20% per crystn.) gave *tri(toluene-o-sulphonyl)melamine*, m. p. 294—295° (Found: C, 49·5; H, 4·1; N, 14·4; S, 16·6. $C_{24}H_{24}O_6N_6S_3$ requires C, 49·0; H, 4·1; N, 14·3; S, 16·3%); it was not sufficiently soluble in camphor for a Rast determination.

*Tribenzenesulphonylmelamine.*—Interaction of *N'*-benzenesulphonyl-*N*-cyanoguanidine (4·5 g., 0·02 mole) and benzenesulphonyl chloride (5·3 g., 0·03 mole) in pyridine (20 ml.) (addition at 15°; spontaneous temperature rise to 60—75°; storage at room temperature for 15 min.), and treatment as previously described gave a white granular solid (7—7·5 g.) which was added to boiling chloroform (50 ml.). The deposited crystalline solid (3—4 g.) was collected; two similar fractions were successively isolated by removal of the solvent under reduced pressure, reprecipitation of the residue from alkaline solution by hydrochloric acid, and dissolution of the dried product in chloroform (total recovery: 5—5·3 g., 69—73%) (final chloroform filtrates A). (*a*) Two crystallisations from ethanol (approx. 15 ml. per g.; recovery per crystn. 70—75%) gave prisms of solvated *tribenzenesulphonylmelamine*, m. p. 149—151° (decomp.) (Found: C, 46·8; H, 4·25. $C_{21}H_{18}O_6N_6S_3,C_2H_6O$ requires C, 46·6; H, 4·05%). (*b*) Alternatively, two crystallisations from ethanol–benzene (15 and 6 ml. per g. respectively; recovery 90%) gave the *melamine* solvated with benzene, m. p. 190—192° (decomp., slight sintering at 187—189°) (Found: C, 52·2; H, 3·7; N, 13·4; S, 15·2. $C_{21}H_{18}O_6N_6S_3,C_6H_6$ requires C, 51·9; H, 3·8; N, 13·5; S, 15·4%).

Heating of solvates (*a*) or (*b*) slowly to 190° during 1 hr., and keeping them at this temperature for a further hour (loss in wt.: 6·9, 10·5%. Calc.: 7·7, 12·5%, respectively), gave *tribenzenesulphonylmelamine*, m. p. 229—231° (decomp.) as a white powder [Found: C, 46·0; H, 3·1; N, 15·4; S, 17·1%; *M* (Rast), 580. $C_{21}H_{15}O_6N_6S_3$ requires C 46·15; H, 3·3; N, 15·4; S, 17·6%; *M*, 546]. Dissolution of this product in ethanol or benzene regenerated the corresponding solvate.

The final chloroform filtrates (A) contained varying quantities of a residue, highly soluble in organic solvents, which could be isolated by precipitation from its alkaline solution by acids. The results of analyses and molecular-weight determinations suggest the presence of a higher polymeric form of benzenesulphonylcyanamide.

*Trimethanesulphonylmelamine.*—Methanesulphonyl chloride (11·45 g., 0·1 mole) was added in four portions at 5-min. intervals to a suspension of *N*-cyano-*N'*-methanesulphonylguanidine (3·24 g., 0·02 mole) in pyridine (25 ml.). The resulting solution was kept at 55—60° for another 30 min., cooled to room temperature, and added to hydrochloric acid (15% w/v, 60 ml.). The brown liquid deposited, after one day's (or occasionally more prolonged) storage at room temperature, deep brown crystals (m. p. 295—298°, decomp.) (1·45—1·75 g., 30—36%). Two crystallisations (carbon) from ethanol (80 ml. per g., recovery: 65%) gave platelets of solvated *trimethanesulphonylmelamine*, m. p. 309—311° (decomp.) (Found: C, 23·4; H, 4·3; N, 19·6; S, 23·4. $C_6H_{12}O_6N_6S_3,C_2H_6O$ requires C, 23·6; H, 4·4; N, 20·7; S, 23·6%), sparingly soluble in water, but not sufficiently soluble in camphor for a Rast determination.

*Hydrolysis of Sulphonylmelamines by Concentrated Sulphuric Acid.*—(*a*) A suspension of finely powdered tri(toluene-*p*-sulphonyl)melamine (2·35 g., 0·004 mole) in concentrated sulphuric acid (6 ml.) was heated to 70°. The resulting pale yellow solution was kept at this temperature for 15 min., and then added to ice (30 g.). The white solid which separated during several hours' storage at 0° was melamine sulphate (0·65 g., 84%) (Found, for specimens recrystallised from water: $SO_4$, 24·8. Calc. for $2C_3H_6N_6,H_2SO_4,2H_2O$: $SO_4$, 24·9%). It was filtered off at 0° (filtrate A), suspended in boiling water (10 ml.), and dissolved by addition of aqueous sodium hydroxide (12% w/w; 1 ml.). The clear (filtered) liquid deposited a white solid (0·28 g., 55%), which gave melamine, m. p. and mixed m. p. 352—354° (decomp.) (from water) (Found: C, 28·5; H, 4·8; N, 66·6. Calc. for $C_3H_6N_6$: C, 28·6; H, 4·8; N, 66·7%). Filtrate A was partly neutralised with aqueous sodium hydroxide (20% w/w; 10 ml.) and treated with a saturated warm solution of *S*-benzyl*iso*thiuronium chloride (3 g.); the precipitated salt was filtered off at 0°, and gave benzylthiuronium toluene-*p*-sulphonate, m. p. and mixed m. p. 178—179° (from aqueous ethanol) (2·43 g., 60%). A control experiment showed that a solution of melamine (0·5 g., 0·004 mole) in concentrated sulphuric acid (6 ml.), kept at 70° for 15 min. and poured into ice-water (30 ml.), gave 85% of melamine sulphate monohydrate.

(*b*) By the same procedure, tri(toluene-*o*-sulphonyl)melamine was hydrolysed to melamine (60%) and benzylthiuronium toluene-*o*-sulphonate (74%), m. p. and mixed m. p. 172—173°.

(*c*) Similarly, tribenzenesulphonylmelamine (containing benzene of crystallisation, m. p. 188—191°) gave melamine (58%) and benzylthiuronium benzenesulphonate (78%), m. p. and mixed m. p. 146—147°.

*Hydrolysis of Sulphonylmelamines by Ethanolic Hydrochloric Acid.*—(*a*) A solution of tri-(toluene-*p*-sulphonyl)melamine (1·18 g., 0·002 mole) in absolute ethanol (150 ml.), saturated with dry hydrogen chloride, was refluxed during 12 hr., a slow stream of hydrogen chloride being continuously passed through the solution. Cyanuric acid gradually appeared in suspension; the liquid was evaporated under reduced pressure to one-third of its volume and cooled to 0°, and the solid collected (0·19 g., 75%) (filtrate A). One crystallisation from water gave cyanuric acid (identified as complex copper salt; Venable and Moore, *J. Amer. Chem. Soc.*, 1917, **39**, 1750) (Found: N, 33·2. Calc. for $C_3H_3O_3N_3$: N, 32·6%). Filtrates A were further evaporated (5—10 ml.) and a trace of cyanuric acid filtered off. On being cooled to 0°, the liquid deposited toluene-*p*-sulphonamide, m. p. and mixed m. p. 136—137° (yield, including material from mother-liquors, 0·84 g., 82%).

(*b*) A suspension of tri(toluene-*o*-sulphonyl)melamine (0·002 mole) gave, on analogous treatment, cyanuric acid (92%) and toluene-*o*-sulphonamide, m. p. and mixed m. p. 152—153° (87%).

(*c*) Trimethanesulphonylmelamine (0·02 mole) gave, after 18 hr.' refluxing, cyanuric acid (72%) and methanesulphonamide, m. p. 87° (59%).

*Other Hydrolysis Attempts.*—Tri(toluene-*p*-sulphonyl)melamine was recovered unchanged (i) after 6 hr.' boiling in 3% aqueous sodium hydroxide or 6% ethanolic potassium hydroxide; (ii) after 5 min.' boiling of its solution in acetic anhydride (15 ml.) containing concentrated sulphuric acid (5 drops).

*Hydrolysis of* N-*Cyano*-N'-*toluene*-p-*sulphonylguanidine.*—(a) *By sulphuric acid.* The compound (4·76 g., 0·02 mole) was dissolved in concentrated sulphuric acid (8 ml.), and the resulting hot solution kept at 70° for 30 min., evolution of carbon dioxide occurring. On dilution with ice (15 g.) and storage at 0°, a crystalline solid was deposited (2·60 g., 56%), which gave guanidine toluene-*p*-sulphonate, m. p. and mixed m. p. 225—226°, after successive crystallisation from small volumes of water and ethanol (Found: C, 41·8; H, 5·9; N, 17·85; S, 13·8. Calc. for $C_8H_{13}O_3N_3S$: C, 41·6; H, 5·6; N, 18·2; S, 13·85%).

(b) *By ethanolic hydrochloric acid.* A solution of the substance (2·38 g., 0·01 mole) in saturated ethanolic hydrochloric acid (150 ml.) was refluxed during 8 hr., and the liquid evaporated to one-third of the original volume under reduced pressure. The crystalline solid which separated on cooling (1·23 g., 48%) was crystallised from ethanol and consisted of toluene-*p*-sulphonylamidinourea, m. p. and mixed m. p. 238—242° (decomp.). The ethanolic filtrates were evaporated nearly to dryness, the residue dissolved in warm water (10 ml.), and the filtered solution made alkaline with ammonia. The collected solid (0·68 g., 32%), crystallised from ethanol, was toluene-*p*-sulphonylguanidine, m. p. and mixed m. p. 203—204°. The aqueous alkaline filtrates contained toluene-*p*-sulphonamide (0·26 g., 15%), m. p. and mixed m. p. 136°, which was isolated by precipitation with acid and crystallised from boiling water.

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## 518. *The Accuracy of Determination of the Magnetic Susceptibility of Solids by the Gouy Method.*

By C. M. French and D. Harrison.

The errors incurred in the determination by various differences in experimental procedure (particularly in methods of packing) and in other factors are examined.

It has frequently been assumed that the accuracy of determination of the magnetic susceptibility of solids, other than homogeneous specimens containing no air or other inclusion, *e.g.*, metal rods, is necessarily appreciably less than that of liquids. This has been ascribed largely to difficulties in packing solids uniformly throughout the volume of the susceptibility tube. However, other factors for which allowance must be made have also been noted, the most important of these being (*a*) a meniscus correction, when a liquid is used to determine the volume of the susceptibility tube, and (*b*) a correction for the presence of air enclosed in the packed solid. The former is considered in detail by Nettleton and Sugden (*Proc. Roy. Soc.*, 1939, *A*, **173**, 313), who, however, do not mention a correction for air present, *i.e.*, they do not differentiate between $d$, the true density of the solid, and $W/V$, where $W$ is the weight of solid packed in a volume $V$ of the susceptibility tube. This, as will subsequently be shown, may give rise to appreciable errors. Hoare (*ibid.*, 1934, *A*, **147**, 88) derived an equation substantially the same as equation (2). His method is, however, open to criticism, in that he assumed that the specific susceptibility of the solid was equal to the measured volume susceptibility of the material in the tube (which may contain an appreciable amount of air) divided by the true density of the solid. Angus and Hill (*Trans. Faraday Soc.*, 1943, **39**, 185), on the other hand, employ the apparent density ($W/V$) of any solid measured. Michaelis and Granick (*J. Amer. Chem. Soc.*, 1943, **65**, 1752), however, make allowance for the presence of air even when paramagnetic solids are under investigation, although the correcting term will here be relatively small. The importance of these various factors, and a simple equation by which they may be taken into account, are discussed below. The method of packing solids is also examined.

*Air enclosed in Packed Solid.*—If $W$ is the weight of solid of density $d$ packed uniformly into a volume $V$ c.c. of tube, then this volume will contain $W/d$ c.c. of solid and $(V - W/d)$ c.c. of air. If $\kappa$ is the susceptibility of 1 c.c. of the solid–air mixture in the tube, then provided the field strength at the top of the specimen is zero, the observed pull $F$ on the specimen of cross-sectional area $A$ will be related to the field strength $H$ at the bottom by the equation $F = \frac{1}{2}(\kappa - \kappa_{air}) . AH^2$. Eliminating $A$ and $H$ from this equation by using a standard substance of known volume susceptibility $\kappa_s$, specific susceptibility $\chi_s$, and density $d_s$, on which the pull under the same conditions is $F_s$, we have

$$\begin{aligned} F_s &= \tfrac{1}{2}(\kappa_s - \kappa_{air}) . AH^2 \\ &= \tfrac{1}{2}(d_s\chi_s - \kappa_{air}) . AH^2 \end{aligned}$$

whence

$$\kappa = (d_s\chi_s - \kappa_{air}) . F/F_s + \kappa_{air}$$

Included in this equation is a contribution of $\kappa_{air}(1 - W/Vd)$, due to the air enclosed in each c.c. of solid–air mixture. Hence the volume susceptibility of the solid itself is

$$\begin{aligned} \kappa_{solid} &= (d_s\chi_s - \kappa_{air}) . F/F_s + \kappa_{air} - \kappa_{air}(1 - W/Vd) \\ &= (d_s\chi_s - \kappa_{air}) . F/F_s + \kappa_{air} . W/Vd \end{aligned}$$

This is the susceptibility of $W/V$ g. of solid, whence the specific susceptibility per g. will be given by

$$\chi = (\chi_s - \kappa_{air}/d_s) . FVd_s/F_sW + \kappa_{air}/d \quad . \quad . \quad . \quad . \quad . \quad (1)$$

*Meniscus Correction.*—Equation (1) can be used without further modification if $V$ is determined directly, by measurement of the cross-sectional area (which must be uniform) and length of tube to a fixed filling mark. Frequently, however, $V$ is determined from the

weight of standard liquid filling the tube to this mark. In this case, $Vd_s$ cannot be equated simply to $W_s$, since the volume of solid packed to the mark will be less than that of the standard liquid by an amount equal to the volume of the meniscus, *i.e.*, $Vd_s = W_s - c$, where $W_s$ is the weight of the standard liquid filling the tube to the mark, and $c$ is the correction for the meniscus effect. Thus, on substitution in equation (1) for $Vd_s$, we have

$$\chi = (W_s - c)(\chi_s - \kappa_{air}/d_s) \cdot F/F_sW + \kappa_{air}/d \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now both the meniscus correction and the ratio of the weight $W_s$ to the length $h$ of the column of liquid filling the tube are functions of the internal radius of the tube (in addition to other variables). It is found that corrections calculated from the Table (based on the data of Bashforth and Adams) given in the International Critical Tables (Vol. I, p. 73, Table 3) may be represented as an approximately linear function of $W/h$, at least in the cases of water, acetone, and benzene, the three liquids commonly used for calibration, and for tubes of radius between 2 and 4 mm., normally employed. Hence the correction for a particular tube can be obtained graphically, or by means of a suitable empirical equation for the particular liquid used; *e.g.*, for benzene (with $W_s$ in g. and $h$ in cm.) from the data in the International Critical Tables (*loc. cit.*), $c = 0{\cdot}0854W_s/h - 0{\cdot}0037$. This meniscus correction has an appreciable effect on the calculated susceptibility of both dia- and paramagnetic substances, and is illustrated in a typical example in the Table.

*Density of Solid.*—The assumption is frequently made that the density of a solid may be represented by the ratio $W/V$, where $W$ is the weight of solid packed as tightly as possible into a volume $V$ of the tube. In the case of paramagnetic solids, except in work of extreme accuracy, the error introduced in making this assumption is generally, though not always, negligible. For example, Michaelis and Granick (*loc. cit.*) give as an example of their method of calculation, their results for Wurster's blue perchlorate, which has a true density of 1·398. However, the apparent density calculated from the weight of solid packed into the susceptibility tube is only 0·308, on account of the loose packing used by these authors. The difference in the calculated value of the susceptibility obtained by using the true and apparent densities is $0{\cdot}0736 \times 10^{-6}$ for this compound ($\chi = 4{\cdot}18 \times 10^{-6}$). With diamagnetic solids the error introduced in making this assumption is frequently appreciable, as illustrated in the Table. Whenever possible, therefore, it is desirable to determine the density of the solid by an independent experiment, and to use this value in the appropriate term of equation (2).

*Method of Packing.*—It is noteworthy that in spite of widely different methods of packing employed by different workers, the values obtained for magnetic susceptibility are often in remarkably good agreement. The reason for this becomes apparent on examination of equation (2). This shows that $F/W$ is the factor having the greatest effect on the value of the susceptibility. Since $\chi$, the susceptibility per g. of solid, must, from its definition, be independent of tightness of packing, then theoretically $F/W$ must also be independent of tightness of packing, since the other terms in equation (2) are unaffected by it. (This assumes, of course, that the true density $d$ of the solid is used for the calculation, since otherwise tightness of packing will influence the magnitude of the $W/V$ term.) Hence the experimentally determined susceptibility should be the same for all methods of packing, provided this is uniform. These conclusions, and the importance of the various factors examined above, are borne out by the data in the following table, which gives values of $10^6\chi$ for a specimen of potassium nitrate (not specially purified).

$V = 4{\cdot}08$ c.c.; $h = 12$ cm.; $F_s = 7{\cdot}94$ mg.; $W_s = 3{\cdot}599$ g.; $\chi_s = -0{\cdot}702 \times 10^{-6}$ (benzene); $c = 0{\cdot}022$ (from graph); $d = 2{\cdot}1$ g./c.c.

| | | *Series* 1. Mean $F = 6{\cdot}34$ mg. Mean $W = 6{\cdot}391$ g. $F/W = 0{\cdot}992$ | | *Series* 2. Mean $F = 5{\cdot}69$ mg. Mean $W = 5{\cdot}730$ g. $F/W = 0{\cdot}993$ | |
|---|---|---|---|---|---|
| Density value | "$W_s$" value | $-10^6\chi$ | Error | $-10^6\chi$ | Error |
| $d$ | $W_s - c$ | 0·315 | 0·000 | 0·315 | 0·000 |
| $W/V$ | $W_s - c$ | 0·310 | −0·005 | 0·308 | −0·007 |
| $d$ | $W_s$ | 0·317 | +0·002 | 0·317 | +0·002 |
| $W/V$ | $W_s$ | 0·312 | −0·003 | 0·310 | −0·005 |

In series 1 the powder was packed by ramming it into the tube in successive, small, approximately equal layers. In series 2 it was loosely packed by tapping the bottom of the tube on the bench after addition of each layer. Although in the second series there is approximately 10% less solid in the tube, there is no significant difference in the $F/W$ ratio. Nevertheless, it frequently appears easier to obtain uniform packing by the method of tight ramming than by other methods, although this may be a personal factor. It is clear, however, that the object of the method adopted must be to obtain uniformity, and not, as is often believed, to remove as much air from the interstices as possible. Correction for the latter factor can be made as previously indicated.

QUEEN MARY COLLEGE, MILE END ROAD, LONDON, E.1. [*Received, March 19th*, 1953.]

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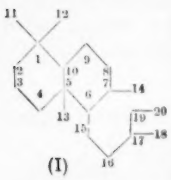
## 519. *The Constitution of Marrubiin. Part I.**

By WESLEY COCKER, B. E. CROSS, S. R. DUFF, J. T. EDWARD, and T. F. HOLLEY.

Spectroscopic and oxidative studies of marrubiin, $C_{20}H_{28}O_4$, indicate that it is a furan derivative, having the structure (III).

MARRUBIIN, a bitter principle of horehound (*Marrubium vulgare* L), is extracted from the herb with acetone in yields of up to 1%, but different samples of the herb produce widely differing amounts, and some samples we examined yielded none. Season of harvesting, conditions of drying, and length of storage have a profound influence upon the yield, and it has been suggested (Rizzocath, Thesis, Univ. Aix-Marseille, 1933) that marrubiin is an artefact arising from an essential oil during the drying of the horehound. It is, of course, important that the herb should be of the correct botanical species. From time to time, *Ballota hirsuta* Bentham has been sold as horehound; this contains little or no marrubiin, which can however be isolated in small yield from *B. foetida* (Balansard, *Compt. rend. Soc. Biol.*, 1934, **117**, 1014). In the present investigation, horehound of Morroccan origin was procured and kindly extracted by Messrs. C. W. Field, Ltd., of Liverpool, to whom we are extremely indebted for valuable co-operation and assistance.

Although earlier workers were engaged on the study of marrubiin, the most significant advances in its chemistry were made by Lawson and Eustice (*J.*, 1939, 587), Holliss, Richards, and Robertson (*Nature*, 1939, **143**, 604), and more recently by Ghigi (*Gazzetta*, 1948, **78**, 865; 1951, **81**, 336). Before Ghigi's publications, it had been shown that marrubiin exhibits the following characteristics and reactions. (*a*) It is a diunsaturated lactone, hydrolysed by alkali to a diunsaturated hydroxy-acid, marrubic acid: reduction of marrubiin and marrubic acid gives the corresponding tetrahydro-compounds. (*b*) It possesses a hydroxyl group incapable of acetylation, but readily removed by dehydrating agents, thus yielding the triunsaturated compound which we now term anhydromarrubiin. For this reason, the hydroxyl is considered to be tertiary. (*c*) The fourth oxygen atom is inert, and probably ethereal. (*d*) On dehydrogenation, marrubiin yields 1 : 2 : 5-trimethylnaphthalene; on the basis of this evidence, and by analogy with the diterpenoid alcohols, Lawson and Eustice (*loc. cit.*) proposed the skeletal structure (I), whilst Holliss, Richards, and Robertson (*loc. cit.*) suggested that marrubiin is a hydroxy-diterpene of the manoyl oxide type. However, marrubiin and its hydro-derivatives differ from manoyl oxide and the closely related sclareol in their inability to form tricyclic derivatives, which can be dehydrogenated to 1 : 2 : 8-trimethylphenanthrene, on treatment with dehydrating agents (cf. Lawson and Eustice, *loc. cit.*; Ruzicka and Janot, *Helv. Chim. Acta*, 1931, **14**, 203; Hosking and Brandt, *Ber.*, 1935, **68**, 37).



(I)

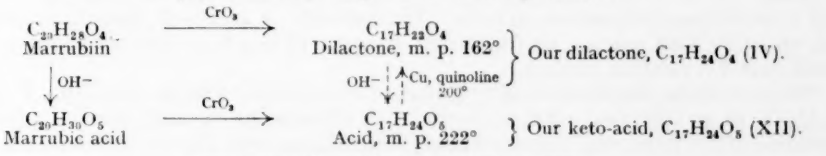
Our investigations, begun in 1949, were well under way when our attention was drawn to the earlier paper by Ghigi (*loc. cit.*). Unfortunately, after some months, a shortage of marrubiin brought our investigations to a standstill until late in 1951. Ghigi's later paper

* Cf. Cocker, Cross, Duff, and Holley, *Chem. and Ind.*, 1952, 827.

contributes little further to the problem, although a number of new derivatives of marrubiin are mentioned. In the earlier paper, she claimed that on oxidation with chromic acid in acetic acid, marrubiin loses three carbon atoms, two double bonds, and the inert oxygen, and yields a lactone, $C_{17}H_{22}O_4$, which can be hydrolysed to an acid, $C_{17}H_{24}O_5$. She claimed further that the latter compound is obtained when marrubic acid is oxidised with either chromic acid or alkaline permanganate (Scheme A). We do not agree with all these conclusions, but we are in agreement that $C_{17}$ compounds are produced in the oxidations and that these compounds yield 1 : 2 : 5-trimethylnaphthalene on dehydrogenation, thus establishing the presence of a bicyclic system in them.

We must now consider what side chain attached to the bicyclic system can lose three carbon atoms, two double bonds, and an inert oxygen atom on oxidation. The light-absorption characteristics and colour reactions of marrubiin strongly suggest that the side chain is a furan, and this would conform with the oxidative evidence.

(A) *Scheme of Ghigi's oxidation experiments.*




—→ Reactions confirmed by the present authors.
- - -→ Reactions contrary to our findings.

In the ultra-violet region, marrubiin shows maxima at 2080, 2120, and 2160 Å (log ε 3·75, 3·75, and 3·70 respectively), in substantial agreement with those expected of a substituted furan (cf. Price and Walsh, *Proc. Roy. Soc.*, 1941, *A*, **179**, 201, who give 1996, 2046, and 2110 Å for furan).

The infra-red spectra of marrubiin and furfuryl alcohol and the published data for furan are :

Marrubiin : 753, 768, 815, 874, 985, 1010, 1045, 1066, 1100, 1155, 1200, 1240, 1270, 1370, 1470, 1505, 1560, 1600, 1665, (1740, 1760, 1765),* 2880, 3440 † cm.$^{-1}$ (* lactonic C=O stretching frequency; † OH stretching frequency).

Furan : 740, 864, 990, 1052, 1176, 1249, 1375, 1495 cm.$^{-1}$ (measurements in liquid phase; Pickett, *J. Chem. Phys.*, 1942, **10**, 660); 605, 744, 837, 872, 994, 1067, 1180, 1270, 1340, 1381, 1486, 1579, 1596 cm.$^{-1}$ (measurement in vapour phase; Thompson and Temple, *Trans. Faraday Soc.*, 1945, **41**, 27).

Furfuryl alcohol : 750, 815, 887, 915, 1010, 1055, 1080, 1148, 1190, 1220, 1260, 1360, 1380, 1510, 1565, 1600, 1680, 2860, 3300 * cm.$^{-1}$ (* OH stretching frequency).

The spectrum of marrubiin is very similar to that of furan and furfuryl alcohol. The absence of the strong " aromatic " absorption in the 750, 1150, and 1470 cm.$^{-1}$ region in tetrahydromarrubic acid (and in tetrahydrofurfuryl alcohol) lends support to the postulate of a furan ring in marrubiin.

Examination of the lactonic C=O stretching frequency of marrubiin shows the presence of a butanolide :

Marrubiin : 1740 cm.$^{-1}$ in paraffin paste; 1760 cm.$^{-1}$ in $CHCl_3$; 1765 cm.$^{-1}$ in $CS_2$.
Anhydromarrubiin : 1760 cm.$^{-1}$ in $CHCl_3$.

Grove and Willis (*J.*, 1951, 877) have shown that butanolides display lactonic C=O stretching frequencies of 1770 cm.$^{-1}$, whilst pentanolides show a corresponding band at 1740 cm.$^{-1}$. It has been found, however, that suspensions in paraffin paste of compounds in which hydrogen bonding is possible, frequently exhibit lower C=O stretching frequencies than are exhibited by solutions of such compounds. We are grateful to Mr. Grove for this information.

Tetrahydromarrubic acid shows strong bands at 3470 (OH) and at 1688 cm.$^{-1}$ ($CO_2H$).

The chemical properties of marrubiin are in harmony with its butanolide structure. Thus, marrubiin is unreactive towards ammonia, aniline, and phenylhydrazine, and

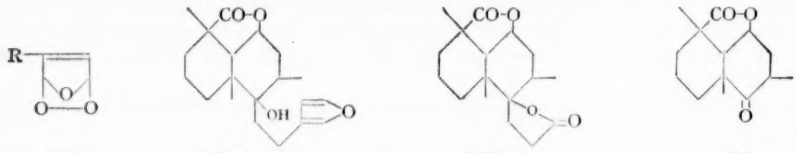
marrubic acid is lactonised by diazomethane. On the other hand, marrubic acid can be acetylated, and must be heated quite strongly before it lactonises, although on long boiling in xylene lactonisation takes place.

So far, we have been unable to obtain much direct chemical evidence in favour of the furan structure. Thus, we have been unable to obtain an adduct with maleic anhydride, nor is the ring hydrogenolysed over copper chromite. Marrubiin, however, smoothly absorbs two mols. of hydrogen over palladised charcoal, but relatively slowly. Hydrogenation over Adams's catalyst is faster, and the rate is in agreement with that expected of a furan (cf. Lawson and Eustice, *loc. cit.*; Jones and Taylor, *Quart. Reviews*, 1950, **4**, 198).

Marrubiin reacts with two mols. of perbenzoic acid, giving a compound which is probably of type (II) (cf. Jones and Taylor, *loc. cit.*), but so far it has proved intractable.

Marrubiin gives a green colour with a mixture of acetic anhydride and sulphuric acid in chloroform, as do furans (Levine and Richman, *Proc. Soc. Exp. Biol., N.Y.*, 1934, **31**, 582), but it fails to give the Shear colour reaction (Levine and Seaman, *Biochem. J.*, 1933, **27**, 2047). Ghigi (1951) claims that a pure coupling product is obtained from the diterpene and *p*-nitrobenzenediazonium chloride. Undoubtedly, a coloured product is obtained but, on an alumina column, we found that it separated into four coloured bands, none of which gave a crystalline product.

When the furan ring is removed by oxidation with chromic acid, we find that a dilactone, $C_{17}H_{24}O_4$, m. p. 160°, $[\alpha]_D$ +30°, is obtained. Evidently the carboxyl group left from the oxidation of the furan ring undergoes ready lactonisation with the tertiary hydroxyl group of marrubiin, which accordingly must be at the $\gamma$-position with respect to the point of attachment of the furan ring, as in (III), and the formula of the dilactone must be (IV).




(II) (III) (IV) (V)

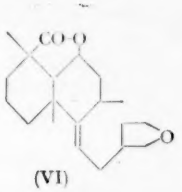
[To economise space, we shall develop our argument by reference to the structure (III) established in the sequel for marrubiin, rather than employ partial formulæ. Our argument involves the reasonable assumption that the skeletal structure of marrubiin is (I), but is otherwise rigorous.] Ghigi obtained by this oxidation a lactone, m. p. 162°, which is almost certainly identical with ours, although she ascribed to it the formula, $C_{17}H_{22}O_4$, and did not recognise it as a dilactone.

Further evidence for the location of the tertiary hydroxyl at $C_{(6)}$ is given by the results of ozonolysis of anhydrotetrahydromarrubiin (Lawson and Eustice, *loc. cit.*) which affords a keto-lactone, $C_{14}H_{20}O_3$, to which we ascribe the formula (V); in this reaction the $C_6$ side chain, including the tetrahydrofuran ring is removed. The keto-lactone exhibits maximum absorption at 2900 Å (log $\varepsilon$ 1·44), and has, amongst others, a band at 1706 cm.$^{-1}$ (cf. Grove and Willis, *loc. cit.*; Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold, New York, 1949, p. 203), both indicative of a ketonic group; a band at 1760 cm.$^{-1}$ indicates the presence of a butanolide, namely, that present in marrubiin. The keto-lactone gives an oxime, but fails to give a semicarbazone (cf. Ruegg, Dreiding, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 889), and is not reduced either with hydrogen and Adams's catalyst or under Clemmensen conditions, indicative of a hindered carbonyl group. The keto-lactone is identical with the unidentified product obtained by Ghigi from the oxidation of anhydromarrubiin with chromic acid. Its formation by ozonolysis indicates that anhydrotetrahydromarrubiin must be (VI), the removal of the tertiary OH at $C_{(6)}$ giving rise to an exocyclic double bond.

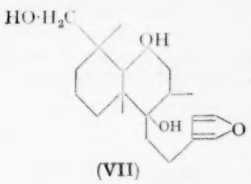
The keto-hydroxy-acid afforded by hydrolysis of the lactone ring is stable in boiling water or alcohol, and so the compound cannot be a $\beta$-keto-acid. Consequently, of the three possible positions, **1**, **5**, and **7**, for the attachment of the carboxyl group to the perhydronaphthalene nucleus, the last two must be excluded, and so the carboxyl group

of this compound, and of marrubic acid, must be at $C_{(1)}$. A second reason for believing the carboxyl group to be at this position is that otherwise a *gem*-dimethyl group would be found at $C_{(1)}$. This is most unlikely in view of the ready aromatisation to naphthalene derivatives (cf. Clemo and Dickenson, *J.*, 1935, 735; 1937, 255; Cocker, Cross, Fateen, Lipman, Stuart, Thompson, and Whyte, *J.*, 1950, 1781). The formation of 1 : 2 : 5-trimethylnaphthalene could be explained only by rather improbable migrations of alkyl groups from the *gem*-position. On the other hand, presence of the carboxyl group at $C_{(1)}$ should lead to ready aromatisation and loss of carbon dioxide.

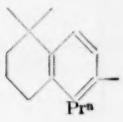
Further evidence against the location of the carboxyl at $C_{(7)}$ (though not necessarily at $C_{(5)}$) is given by facts pointing to its attachment to a tertiary carbon atom. Thus, (*a*) heating marrubic acid with concentrated sulphuric acid yields carbon monoxide (cf. Fieser and Fieser, *op. cit.*, p. 52); and (*b*) marrubic acid resists esterification, so that diazomethane lactonises it, even in cold ether, to marrubiin.




(VI)




(VII)




(VIII)

We have attempted to confirm the position of the carboxyl group by the methods applied by Ruzicka and Meyer (*Helv. Chim. Acta*, 1922, **5**, 581) to the resin acids. Reduction of marrubiin or marrubic acid with lithium aluminium hydride yields the triol, marrubenol, $C_{20}H_{32}O_4$ (VII), which is reduced catalytically to a tetrahydro-compound, marrubanol, $C_{20}H_{36}O_4$. This compound can also be obtained by the reduction of tetrahydromarrubiin. Dehydrogenation of marrubenol yields, with difficulty, a small amount of 1 : 2 : 5-trimethylnaphthalene. Attempts to rearrange and dehydrate marrubanol with anhydrous formic acid, polyphosphoric acid, or hydrochloric acid in acetic acid gave intractable gums. Dehydrogenation of these products with sulphur, selenium, or palladised charcoal failed to give the expected 5-ethyl-1 : 2-dimethylnaphthalene. Instead a benzenoid hydrocarbon, probably (VIII), was obtained.

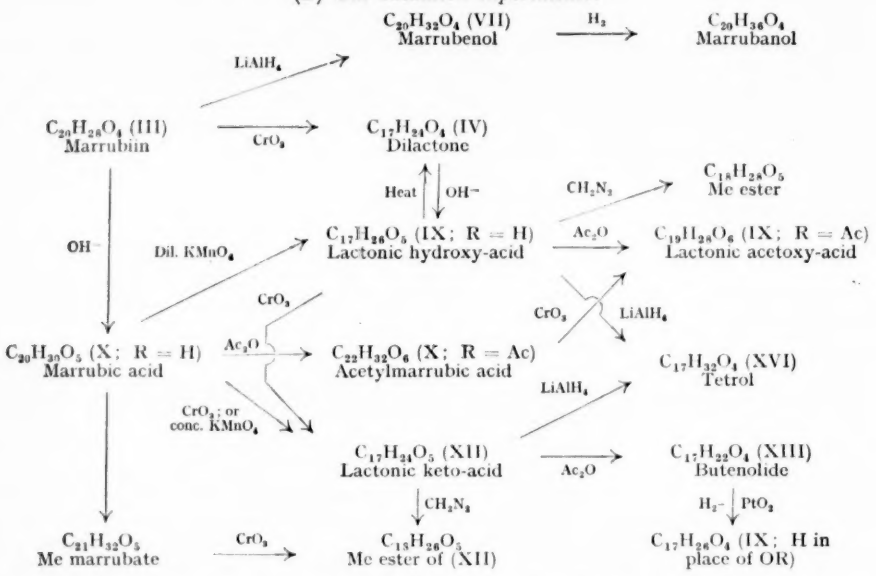
When the dilactone (IV), $C_{17}H_{24}O_4$, is hydrolysed, one lactone ring is opened and a lactonic hydroxy-acid, $C_{17}H_{26}O_5$, m. p. 205°, $[\alpha]_D^{16}$ −15°, showing the characteristic absorption by hydroxyl at 3300 cm.$^{-1}$, is obtained. This acid neutralises one equivalent of alkali in the cold, but by hydrolytic titration consumes two equivalents, showing it to be a lactonic acid. Ghigi claimed that hydrolysis of her lactone, $C_{17}H_{22}O_4$, gave an acid, $C_{17}H_{24}O_5$, m. p. 222°, also afforded by the oxidation of marrubic acid with chromic acid. As we show below, this oxidation yields a lactonic keto-acid, m. p. 220°, $[\alpha]_D^{23}$ +88·7°. The melting point of the lactonic hydroxy-acid is markedly influenced by rate of heating, and we have obtained melting points above 210° by rapid heating. It is possible that the closeness of the melting points and analytical values led Ghigi to confuse these two acids.

The lactone ring opened by the hydrolysis is the one originally present in marrubiin, so the acid must have the structure (IX; R = H). This follows from the facts, (*a*) that it also arises in low yield from the oxidation of marrubic acid (X; R = H) with dilute permanganate, and (*b*) that its acetyl derivative (IX; R = Ac) is obtained on oxidation of acetylmarrubic acid, which must have formula (X; R = Ac) since the tertiary hydroxyl is incapable of being acetylated (Lawson and Eustice, *loc. cit.*). Obviously in both of these reactions a dicarboxylic acid intermediate (XI; R = H and Ac) is involved, which undergoes ready lactonisation between the 6-hydroxyl and the 17-carboxyl group noted previously. When the hydroxy-acid (IX; R = H) is heated with acetic anhydride, formation of the second lactone ring proceeds, yielding the dilactone (IV).

When marrubic acid is oxidised with chromic acid, or with concentrated permanganate solution, or when the lactonic hydroxy-acid (IX; R = H) is oxidised with chromic acid,

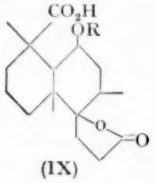
the lactonic keto-acid, $C_{17}H_{24}O_5$ (XII), m. p. 220°, $[\alpha]_D$ +88·7°, is formed. Ghigi obtained an uncharacterised acid, $C_{17}H_{24}O_5$, from the oxidation of marrubic acid. The presence in the acid of a six-membered ring ketone is shown by an absorption band at 1736 cm.$^{-1}$; the butanolide C=O gives rise to a band at 1758 cm.$^{-1}$, and the carboxyl C=O to one at 1672 cm.$^{-1}$; a strong band at 1460 cm.$^{-1}$ may be due to the carboxylate ion (cf. Thompson, *J.*,

(B) *Our oxidation experiments.*

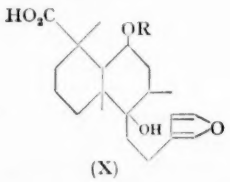



1948, 328). In the ultra-violet the acid exhibits a maximum at 2580 Å (log ε, 1·69); this is an unusually short wave-length and high intensity for an isolated keto-group, but no other reasonable absorbing system can be ascribed to it; possibly the neighbouring carboxyl group, rigidly anchored close to it, has a profound effect on the electronic mobility. That the keto-group is strongly hindered is shown by the formation of an oxime, but not a semicarbazone.

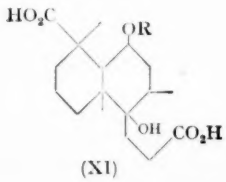
That the carboxyl group of (XII) is the original carboxyl group of marrubic acid is shown by the fact that methyl marrubate affords on oxidation a methyl ester identical with that formed by esterification of (XII).




(IX)




(X)

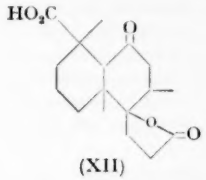



(XI)

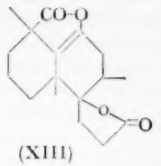
Cyclisation of (XII) with acetic anhydride affords a butenolide (XIII), $C_{17}H_{22}O_4$, m. p. 148—150°, $[\alpha]_D^{17}$ −132°. Ghigi, however, claimed that the product of oxidation of marrubic acid with chromic acid is cyclised to a lactone identical with that obtained from the oxidation of marrubiin. The latter product is, in fact, the dilactone (IV), completely different from the butenolide (see Scheme B). That our cyclisation product is a βγ-butenolide is shown by its properties: it rapidly decolorises bromine and permanganate solutions; its solution in warm water has pH 3—4 and after 10 hours' boiling in water the lactone and keto-acid are present in solution in the ratio 2 : 1; it is completely

hydrolysed by boiling 2% aqueous methanolic hydrochloric acid; it gives a keto-anilide when kept in aniline (cf. Kuehl, Linstead, and Orkin, *J.*, 1950, 2213); and it is reduced over Adams's catalyst to a saturated acid, $C_{17}H_{26}O_4$, to which we assign structure (IX; H in place of OR). The last reaction, involving hydrogenolysis of the lactone, is characteristic of βγ-butenolides (cf. Jacobs and Scott, *J. Biol. Chem.*, 1930, **87**, 601; 1931, **93**, 139). The βγ-butenolide shows no tendency to isomerise to the αβ-form, evidence supporting the thesis that the lactonic CO group is attached to a tertiary carbon atom as in (XIII).

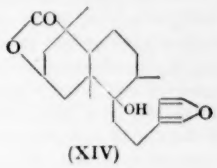
The proof that the βγ-butenolide, $C_{17}H_{24}O_5$, has the structure (XIII) is clearly fundamental in deciding the formula for marrubiin. A butanolide of carbon skeleton (I) and having the lactone C=O attached at $C_{(1)}$, can have its other oxygen atom only at $C_{(3)}$ or $C_{(9)}$ as in (III) and (XIV) respectively. Attachment to $C_{(3)}$, resulting in the structure (XIV) for marrubiin, is sterically possible; but it would give rise to the sterically impossible structure (XV) for the butenolide mentioned above. The latter must consequently have the structure (XIII),* and the corresponding keto-acid the structure (XII). Furthermore, it can readily be seen that a pentanolide structure for marrubiin, which would locate the oxygen of the lactone ring at $C_{(4)}$ or $C_{(8)}$, is impossible because the formation of a pentenolide from the keto-acid, $C_{17}H_{24}O_5$, would be stereochemically impossible.



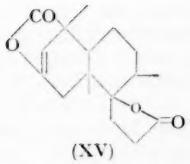
(XII)



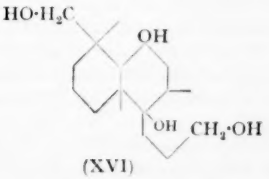
(XIII)



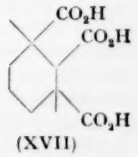
(XIV)



(XV)



(XVI)



(XVII)

Reduction of either of the $C_{17}$-acids yields the same tetrahydroxy-compound (XVI), $C_{17}H_{32}O_4$, a result to be expected of acids bearing the relationship expressed above. It was heated with various dehydrating agents, but no crystalline product could be isolated. The product from an attempted rearrangement with hydrochloric acid in acetic acid was, therefore, dehydrogenated with palladised charcoal to a hydrocarbon, $C_{16}H_{24}$. Its spectrum displayed maxima at (2210), 2680, and (2890) Å (log ε 3·99, 2·92, 2·75), similar to the spectrum of a tetra-alkyl substituted benzene, *e.g.*, prehnitene (cf. Amer. Petroleum Inst. Res. Project No. 44, Nat. Bur. Standards, Washington), and is probably (VIII). Such a compound would be expected to resist aromatisation (cf. Clemo and Dickenson, *loc. cit.*; Cocker *et al.*, *loc. cit.*).

Further work is in progress and attempts are being made to degrade marrubiin to the tricarboxylic acid (XVII), already obtained from abietic acid. This would also enable the stereochemistry of the first ring to be elucidated; work on these lines is being pursued.

## Experimental

*Extraction of Marrubiin* (III) (cf. Mercier and Mercier, *Compt. rend.*, 1932, **195**, 1102; Ghigi, 1948, *loc. cit.*).—Powdered horehound (10 lb.) was extracted in a continuously operating apparatus with cold acetone (14 l.) for 48 hr.; the acetone was concentrated to 1 l., and the solution was filtered. The filtrate was evaporated to dryness and the residue set aside with

* The exocyclic $\Delta^8$-butenolide is also sterically possible: a decision on the exact position of the double bond awaits further evidence.

ether (1 l.) for 15 hr., thus removing waxes and chlorophyll and leaving a residue of impure marrubiin (45 g.). This was dissolved in 5% alcoholic sodium hydroxide (300 c.c.), boiled for 10 min., and poured into a large excess of water. The precipitated marrubiin (30 g.) was collected and crystallised from alcohol as prisms (25 g.), m. p. 160°, $[\alpha]_D^{20}$ +35·8° (*c*, 3·1 in $CHCl_3$).

Marrubic acid (X; R = H) (Lawson and Eustice, *loc. cit.*) had $[\alpha]_D^{15}$ +8·81° (*c*, 1·01 in MeOH).

*Oxidation of Marrubiin with Chromic Acid to the Dilactone*, $C_{17}H_{24}O_4$ (IV).—Carried out essentially in accordance with the procedure of Ghigi (*loc. cit.*), this afforded the dilactone, m. p. 160°, $[\alpha]_D^{16}$ +30° (*c*, 1·2 in $CHCl_3$) (Found: C, 69·2; H, 8·3. Calc. for $C_{17}H_{24}O_4$: C, 69·9; H, 8·2. Calc. for $C_{17}H_{22}O_4$: C, 70·4; H, 7·7%). Ghigi reported m. p. 162° for a compound $C_{17}H_{22}O_4$.

*Ozonolysis of Marrubiin* (cf. Holliss, Richards, and Robertson, *loc. cit.*).—Marrubiin (5 g.) in acetic acid (100 c.c.) was ozonised with 5% ozone, and the solvent then removed in a vacuum. The oily product, dissolved in methyl alcohol, deposited a dilactone (0·9 g.), m. p. 157—159°, undepressed by the previous compound.

*Lactonic Hydroxy-acid*, $C_{17}H_{26}O_5$ (IX; R = H).—(a) *By hydrolysis of the dilactone*, $C_{17}H_{24}O_4$. The dilactone (0·7 g.) was refluxed in 10% methyl-alcoholic potassium hydroxide (10 c.c.) for 4·5 hr. After removal of the alcohol, the *hydroxy-acid* was liberated with hydrochloric acid, removed with chloroform, and crystallised from ethyl acetate as plates, m. p. 205—207°, $[\alpha]_D^{16}$ −15·0° (*c*, 1·56 in $CHCl_3$) (Found: C, 65·6; H, 8·3%; equiv., 338. $C_{17}H_{26}O_5$ requires C, 65·8; H, 8·3%; equiv., 310). Hydrolytic titration gave an equivalent wt. 141. The acid was relactonised by heating it with acetic anhydride and sodium acetate on the water-bath, and purifying the product on an alumina column (benzene). The *methyl* ester * of the hydroxy-acid, prepared in ether with diazomethane, crystallised from alcohol in plates, m. p. 154°, $[\alpha]_D^{19}$ −18·8° (*c*, 0·7 in $CHCl_3$) (Found: C, 66·3; H, 8·5; active H, 0·31. $C_{18}H_{28}O_5$ requires C, 66·7; H, 8·6; 1 H, 0·31%).

(b) *By oxidation of marrubic acid with dilute aqueous permanganate solution.* Marrubic acid (15 g.), dissolved in N-sodium hydroxide (45 c.c.) and diluted to 750 c.c., was treated dropwise with 5% aqueous potassium permanganate (182 c.c.), and the mixture was stirred for 1 hr. It was heated on the water-bath for 10 min., then filtered, the filtrate extracted with ether, and the aqueous layer treated with sulphur dioxide to remove marrubic acid. This was collected, and the filtrate was acidified with hydrochloric acid and extracted with ether from which the acid (3 g.) was obtained.

*Dehydrogenation of the Lactonic Hydroxy-acid.*—The acid (2·5 g.) was heated with palladised charcoal (2·5 g.) at 260° for 48 hr. A pungent acetic acid-like smell was noticed. From the reaction a colourless oil (0·2 g.), b. p. 120°/22 mm., was obtained. It yielded a picrate, m. p. 139—140°, and trinitrobenzene adduct, m. p. 159—160°, undepressed by the picrate and trinitrobenzene adduct, respectively, of 1 : 2 : 5-trimethylnaphthalene.

*Acetoxy-lactonic Acid*, $C_{19}H_{28}O_6$ (IX; R = Ac).—(a) *By acetylation of the lactonic hydroxy-acid*, $C_{17}H_{26}O_5$. Acetylation with pyridine–acetyl chloride for 14 hr. at room temperature afforded the *acetoxy-acid*, crystallising from *cyclo*hexanone as plates, m. p. 246°, $[\alpha]_D^{13}$ −15·1° (*c*, 0·74 in $CHCl_3$) (Found: C, 64·6; H, 7·9. $C_{19}H_{28}O_6$ requires C, 64·8; H, 8·0%). The *methyl* ester of the acetoxy-acid, prepared with diazomethane, crystallised from methyl alcohol as plates, m. p. 133° (Found: C, 65·4; H, 8·7. $C_{20}H_{30}O_6$ requires C, 65·6; H, 8·2%).

(b) *By oxidation of acetylmarrubic acid with chromic acid.* Acetylmarrubic acid, m. p. 112°, $[\alpha]_D^{15}$ −20·7° (*c*, 0·8 in MeOH) (6 g.), in acetic acid (30 c.c.) was treated with chromic acid (15 g.) in water (20 c.c.) and acetic acid (80 c.c.), added slowly at room temperature. After 72 hr. the acetic acid was removed under reduced pressure, and the residue treated with hydrochloric acid and extracted several times with ether. The acetoxy-acid removed from the ethereal solution by extraction with carbonate solution was identical with the product described above (m. p. and mixed m. p.) (Found: C, 64·8; H, 8·1%).

*Lactonic Keto-acid*, $C_{17}H_{24}O_5$ (XII).—This compound was prepared by the oxidation of marrubic acid (cf. Ghigi, *loc. cit.*) or the lactonic hydroxy-acid, $C_{17}H_{26}O_5$, with chromic acid in acetic acid. It had m. p. 222—223°, $[\alpha]_D^{23\cdot5}$ +88·7° (*c*, 2·4 in $CHCl_3$) (Found: C, 66·0; H, 7·55. $C_{17}H_{24}O_5$ requires C, 66·2; H, 7·8%). Its *methyl* ester, had m. p. 164°, not 154° as described by Ghigi (Found: C, 67·4; H, 8·2; OMe, 10·75. $C_{18}H_{26}O_5$ requires C, 67·1; H,

* This is probably the ester obtained by Ghigi on the oxidation of marrubic acid and esterification of the product.

8·1; OMe, 9·7%). Its *oxime* had m. p. between 260° and 280° (decomp.) according to rate of heating (Found: N, 4·45. $C_{17}H_{25}O_5N$ requires N, 4·3%). It gave no ferric colour. The *oxime* of the methyl ester had m. p. 187—189° (Found: C, 63·9; H, 7·9. $C_{18}H_{27}O_5N$ requires C, 64·1; H, 8·0%).

*Methyl Ester of the Lactonic Keto-acid obtained by Oxidation of Methyl Marrubate.*—Methyl marrubate was obtained as follows. A mixture of marrubic acid (2 g.) and alcohol (30 c.c.), containing potassium hydroxide (0·32 g.), was evaporated to dryness, and the residue was heated with methyl iodide (30 c.c.) and anhydrous potassium carbonate (2·0 g.) in a sealed tube at 100° for 3 hr. and at 150° for a further 1 hr. The product crystallised from light petroleum as plates (1 g.), m. p. 84—85° (cf. Hole *et al.*, *loc. cit.*), $[\alpha]_D^{15}$ 0° (*c*, 0·8 in MeOH). The ester (2·7 g.) in acetic acid (20 c.c.) was treated with chromic acid (6·5 g.) in water (10 c.c.) and acetic acid (50 c.c.), added dropwise with stirring, at room temperature. The mixture was left for 72 hr., the acetic acid removed in a vacuum, and the residue treated with 18% hydrochloric acid (50 c.c.) and then extracted several times with ether. The extract, washed first with sodium carbonate solution and then with water, yielded a solid which, crystallised (0·8 g.) from alcohol, had m. p. 162°, undepressed by a specimen of the methyl ester of the lactonic keto-acid mentioned above.

*Preparation of the Unsaturated Lactone,* $C_{17}H_{22}O_4$ (XIII), *of the Lactonic Keto-acid.*—The lactonic keto-acid was refluxed in acetic anhydride–sodium acetate for 1·5 hr. The unsaturated *lactone*, isolated by the usual methods after removal of the acetic anhydride at reduced pressure, crystallised from aqueous alcohol as needles, m. p. 148—150°, $[\alpha]_D^{17}$ −132° (*c*, 0·5 in $CHCl_3$) (Found: C, 70·3; H, 7·4. $C_{17}H_{22}O_4$ requires C, 70·3; H, 7·6%). It readily absorbed bromine and decolorised methanolic permanganate. Treated with aniline in the cold for 36 hr. it gave an *anilide* (needles from aqueous methyl alcohol), m. p. 196° (Found: C, 71·8; H, 7·6. $C_{23}H_{29}O_4N$ requires C, 72·1; H, 7·6%). When 0·1 g. of lactone was boiled with 20 c.c. of water for 10 hr. it yielded unchanged lactone (0·05 g.), and keto-acid (0·025 g.). Reduced in acetic acid (0·5 g. in 30 c.c.), over Adams's catalyst (0·1 g.), the lactone gave a semi-solid product which was extracted with dilute sodium carbonate, yielding unchanged unsaturated lactone (0·2 g.) and a saturated *acid* (0·15 g.), m. p. 262—264° (needles from dilute methyl alcohol) (Found: C, 69·4; H, 8·9. $C_{17}H_{26}O_4$ requires C, 69·4; H, 8·8%).

*Ozonolysis of Anhydrotetrahydromarrubiin.*—This compound (Lawson and Eustice, *loc. cit.*), $[\alpha]_D^{21}$ +51·4° (*c*, 2·0 in MeOH), from 10 g. of marrubiin, was ozonised in ethyl acetate at −5°, and the product was hydrogenated over palladised charcoal. A gum was obtained which on refluxing with ether yielded a *keto-lactone* (V) (1·3 g.), and this crystallised from methyl alcohol as needles, m. p. 195°, $[\alpha]_D^{15}$ +118·6° (*c*, 1·06 in $CHCl_3$) (Found: C, 70·7; H, 8·5. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%). Its *oxime* (feathery needles from dilute alcohol) had m. p. 182—183° (Found: N, 5·20. $C_{14}H_{21}O_3N$ requires N, 5·6%) and gave no ferric colour. On hydrolysis with 10% methyl-alcoholic potassium hydroxide, the keto-lactone yielded an *acid*, m. p. 172—174° (needles from methyl alcohol) $[\alpha]_D^{22}$ −30·9° (*c*, 2·0 in MeOH) (Found: C, 66·1; H, 8·5. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7%).

*Oxidation of Anhydromarrubiin.*—The crude anhydro-compound (10 g.), prepared by Lawson and Eustice's method (*loc. cit.*), was warmed on the water-bath with chromic oxide (20 g.) in acetic acid (100 c.c.) and gave the above keto-lactone (0·4 g.), m. p. and mixed m. p. 195°.

*Dehydrogenation of the Keto-lactone.*—This compound (0·55 g.) was heated for 20 hr. at 300—320° with selenium (1·2 g.) and yielded an oil (0·06 g.; b. p. 110°/2 mm.), which failed to give a picrate.

*Marrubenol* (VII).—Marrubiin (20 g.) in a Soxhlet thimble was refluxed (18 hr.) with lithium aluminium hydride (12 g.) in dry ether (200 c.c.). The product was decomposed in the usual way. The *triol* (19 g.) crystallised from dilute alcohol in needles, m.p. 138°, $[\alpha]_D^{15}$ +19·9° (*c*, 1·1 in MeOH) (Found: C, 71·2; H, 9·4. $C_{20}H_{32}O_4$ requires C, 71·4; H, 9·5%).

*Marrubanol.*—The preceding compound (10·5 g.) was reduced in acetic acid (200 c.c.) over Adams's catalyst (0·5 g.). The product crystallised from dilute alcohol as rhombs (4 g.), m. p. 175°, $[\alpha]_D^{20}$ +15·15° (*c*, 2·0 in MeOH) (Found: C, 70·8; H, 11·2. $C_{20}H_{36}O_4$ requires C, 70·6; H, 10·6%).

*Attempted Dehydration of Marrubanol, and Dehydrogenation of the Product.*—Marrubanol (7·6 g.) was heated with anhydrous formic acid (27 g.) for 4 hr., and the mixture poured into water. The yellow oil was collected (4·8 g.) and distilled, yielding two fractions: (*a*) (1·2 g.), b. p. 154°/2 mm. (Found: C, 79·4; H, 10·6. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·5%); and (*b*) (1·6 g.) (Found: C, 77·2; H, 9·9%). Fraction (*a*) was heated with palladised charcoal (1·2 g.) at 22° for 19 hr., and at 260° for a further 29 hr. The *product* consisted of an oil (0·4 g.; b. p.

119°/2 mm.) (Found: C, 86·6; H, 11·1. $C_{16}H_{24}$ requires C, 88·8; H, 11·2%). It failed to give a picrate.

*Reduction of the $C_{17}$ Acids and Esters with Lithium Aluminium Hydride.*—The acids (6 g.), or equivalent quantities of ester, were refluxed in a Soxhlet apparatus with lithium aluminium hydride (3·2 g.) in ether (550 c.c.) for 4 days, and the product worked up in the usual way. A gum (2·5 g.), which slowly solidified, was obtained; the *tetrol* (XVI), crystallised first from acetone and then methyl alcohol, had m. p. 193—194°, $[\alpha]_D^{14}$ +19·8° (*c*, 1·2 in MeOH) (Found: C, 67·6, 67·9; H, 10·8, 10·7. $C_{17}H_{32}O_4$ requires C, 68·0; H, 10·7%) and was very sparingly soluble in ether.

*Dehydration of the Alcohol and Aromatisation of the Product.*—The alcohol (2·4 g.), dissolved in a mixture of glacial acetic acid (25 c.c.) and concentrated hydrochloric acid (25 c.c.), was set aside overnight. The ice-cold solution was then saturated with hydrogen chloride, set aside for 1 hr., and finally heated on the water-bath for 3·5 hr. The mixture was poured into water and extracted with ether, and the extract washed with sodium carbonate solution. Removal of the ether yielded an intractable gum which was dehydrogenated with palladised charcoal (3 g.) for 48 hr. at 250—260°. The product (0·5 g.) was fractionated over sodium, yielding a colourless oil, b. p. 125°/12 mm. (Found: C, 88·6; H, 11·3. $C_{16}H_{24}$ requires C, 88·9; H, 11·1%). This is probably the *compound* (VIII).

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TRINITY COLLEGE, DUBLIN. [*Received, March 25th*, 1953.]

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## 520. *The Chemistry of the Triterpenes and Related Compounds. Part XVIII.* Elucidation of the Structure of Polyporenic Acid C.*

By A. BOWERS, T. G. HALSALL, E. R. H. JONES, and (in part) A. J. LEMIN.

Polyporenic acid C has been characterised as a triethenoid tetracyclic hydroxy-keto-carboxylic acid with the formula $C_{31}H_{46}O_4$. Its structure (XXXIV) has been finally established by conversion into a derivative of eburicoic acid which has in turn been converted (Holker, Powell, Robertson, Simes, Wright, and Gascoigne, *J.*, 1953, 2422) into a lanosterol derivative. Eburicoic acid and polyporenic acid C can be regarded as derivatives of trimethylergostane. It is of particular interest that the carbon skeleton of the side chains is identical with that of the major fungal sterol, ergosterol, suggesting some common paths in their biosynthesis.

IN 1939 Cross, Eliot, Heilbron, and Jones (*J.*, 1940, 632) carried out a re-investigation of the constituents of the birch tree fungus, *Polyporus betulinus* Fr., which led to the isolation of polyporenic acids A, B, and C. It was suggested that these acids might be triterpenoids and in the case of polyporenic acid C a formula $C_{30}H_{46}O_4$ or $C_{30}H_{48}O_4$ was suggested on the basis of an analysis of methyl polyporenate C, m. p. 192—193°. The work was abandoned in 1940 and it is only recently that it has become possible to examine polyporenic acid C in detail.

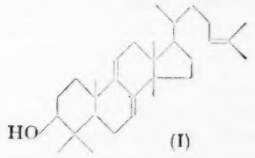
In the interval only one communication relating to polyporenic acid C has appeared. Birkinshaw, Morgan, and Findlay (*Biochem. J.*, 1952, **50**, 509) have described the isolation of an acid ($C_{30}H_{46}O_4$), m. p. 285—290°, from the metabolic products of the wood-rotting fungus *Polyporus benzoinus* (Wahl) Fr. The acid gave colour reactions characteristic of triterpenoid acids and was converted into a neutral monomethyl ester, m. p. 192—193°. Ozonolysis of the acid afforded a 53% yield of formaldehyde. It was suggested that the

* Part XVII, *J.*, 1953, 590.

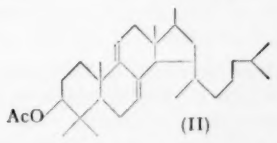
acid was a dihydroxy-monocarboxylic acid possessing a vinylidene group. Further, attention was drawn to the possibility that the acid might be polyporenic acid C and this was enhanced when a sample of methyl polyporenate C showed no depression in melting point on admixture with the methyl ester of the *P. benzoinus* acid. Through the courtesy of Dr. J. H. Birkinshaw it has been possible for us to compare the infra-red spectra of the methyl esters of polyporenic acid C and of the *benzoinus* acid. They are identical and it may be concluded that the *benzoinus* acid is very probably polyporenic acid C. However, for reasons which appear in the sequel, our conclusions about the nature of polyporenic acid C differ from those drawn by Birkinshaw *et al.* (*loc. cit.*).

At first great difficulty was experienced in isolating appreciable quantities of acid C, partly owing to the lack of a suitable method of estimating it in impure samples. This handicap was overcome when methyl polyporenate C was found to contain a conjugated diene system and the purification of the acid could be followed by spectrographic examination. The further discovery that polyporenic acid C contained a keto-group (see below) enabled a satisfactory method for its isolation based on a Girard separation to be developed.

Pure methyl polyporenate C, m. p. 198—199°, analysed for either $C_{31}H_{46}O_4$ or $C_{32}H_{48}O_4$, and showed maximal light absorption at 2360, 2430, and 2510 Å ($\varepsilon$ = 14,600, 16,900, and 11,200 respectively). These values, indicating the presence of a heteroannular diene system, are very similar to those of methyl dehydroeburicoate and of dehydrolanosterol (I), and different from those of dehydroeuphenyl acetate (II) (cf. Dawson, Halsall, and Swayne, *J.*, 1953, 590). This suggested that the lanostane ring system (III) might be present in polyporenic acid C. It seemed possible that polyporenic acid C might be dehydropolyporenic acid A, especially in view of the co-existence of eburicoic acid and dehydroeburicoic acid in a number of fungi (Gascoigne, Holker, Ralph, and Robertson, *J.*, 1951, 2346). However, the ultra-violet spectrum of methyl polyporenate C indicated the presence of a keto-group (inflexion at 2760—2820 Å, $\varepsilon$ = 57), and a 2 : 4-dinitrophenylhydrazone was prepared. Determination of the infra-red spectrum in carbon tetrachloride revealed a band at 1712 cm.$^{-1}$, indicative of a keto-group in either a six-membered ring or an aliphatic side chain. The infra-red spectrum also had bands at 3641 cm.$^{-1}$, and at 891 and 1639 cm.$^{-1}$, indicative of hydroxyl and vinylidene groups respectively. Thus methyl




(I)

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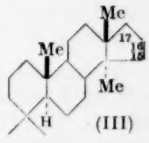



(III)

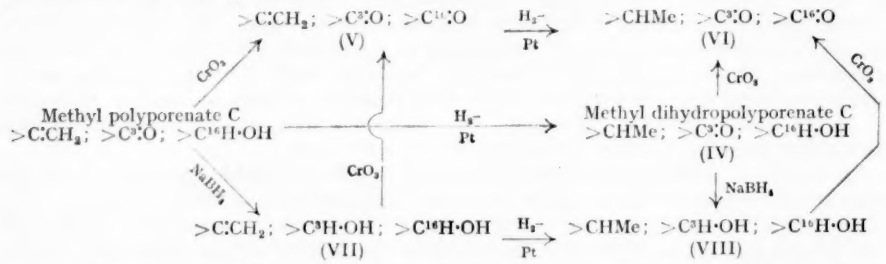
polyporenate C could be formulated as the ester of a hydroxy-keto-acid. The analytical data did not enable a clear-cut decision to be made between $C_{31}H_{46}O_4$ and $C_{32}H_{48}O_4$ for the ester, but, if the presence of three double bonds is assumed, both possibilities indicated the tetracyclic nature of polyporenic acid C. As will become clear in the sequel the correct formula of the acid is $C_{31}H_{46}O_4$ and that of the methyl ester, $C_{32}H_{48}O_4$.

Ozonolysis of methyl polyporenate C gave formaldehyde, isolated in 44% yield as its dimethone. Hydrogenation gave methyl dihydropolyporenate C, showing the same ultra-violet absorption as the parent ester, but no absorption in the infra-red corresponding to a vinylidene group. Thus the latter group was not part of the diene system, and the presence of three double bonds in acid C was confirmed.

Hydrolysis of the methyl ester was not as easy as with methyl polyporenate A, heating under reflux with 10% methanolic potassium hydroxide for 16 hr. being necessary. This indicated some hindrance of the carboxyl group although not as intense as that in, for example, oleanolic acid. Acetylation of the acid gave only a monoacetate and no evidence of the formation of a diacetate was obtained.

The simple oxidation, reduction, and hydrogenation reactions which have been carried out starting from the methyl ester are summarised schematically below. The diene system remained unaffected during these transformations. The systematic nomenclature

of the various products on the basis of eburicane for the saturated parent hydrocarbon is given in the Experimental section.

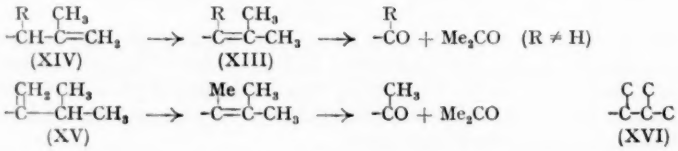



The ultra-violet spectrum of the diketo-ester (V), obtained by oxidation of methyl polyporenate C, showed that the diene system was not conjugated with a keto-group. The original hydroxyl group cannot therefore be in a position α to the diene system. Further evidence about its location was provided by the infra-red spectrum of the diketo-ester which had an additional band at 1743 cm.$^{-1}$ due to the new keto-group derived from the original hydroxyl group. This must therefore be attached to a five-membered ring (Jones *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 2024).

Sodium borohydride treatment of the diketo-esters (V and VI) derived from methyl polyporenate C and methyl dihydropolyporenate C effected preferential reduction of the original, and apparently less hindered, keto-group with the formation of the keto-alcohols (IX) and (X) respectively. Hydrogenation of the alcohol (IX) gave (X), and acetylation of both gave monoacetates. The products of these selective borohydride reductions showed no infra-red absorption band corresponding to a carbonyl group in a six-membered ring. It is therefore the keto-group in the five-membered ring arising from the original (16-)hydroxyl group, which is apparently somewhat more hindered than the original (3-)keto-group in the six-membered ring.

Dehydration of the sodium borohydride reduction product (X) with phosphorus pentachloride in light petroleum gave a product which on ozonolysis yielded acetone, isolated in 75% yield as its 2 : 4-dinitrophenylhydrazone. Analogous dehydrations are well known with triterpenes having partial structure (XI) (cf. Christen, Dünnenberger Roth, Heusser,

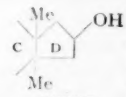
and Jeger, *Helv. Chim. Acta*, 1952, **35**, 1757) and it was concluded that polyporenic acid C possessed a typical triterpene ring A but containing a keto-group as in (XII), and that reduction of the keto-group gave a hydroxyl group with the normal β-configuration (*i.e.*, XI).




Polyporenic acid C, in contrast to polyporenic acid A, was not decarboxylated on melting, making a βγ-unsaturated acid formula improbable. The unconjugated double bond on the other hand migrated under acidic conditions; treatment of a chloroformic

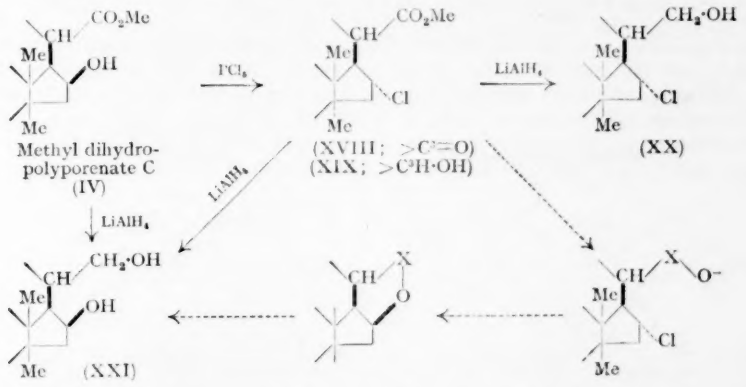
solution of methyl polyporenate C with hydrogen chloride gave an *iso*-compound (methyl *iso*polyporenate C; double bond as in XIII), ozonolysis of which gave acetone and a neutral compound, not oxidised further by chromic acid in acetone. These results suggested that the neutral component was a ketone rather than an aldehyde and were consistent with the structures (XIV) and (XV). Either structure is consistent with the presence in polyporenic acid C of a side chain terminating with the carbon skeleton (XVI).

In an attempt to dehydrate methyl dihydropolyporenate C, it was treated with phosphorus pentachloride. Instead of elimination occurring, the hydroxyl group was replaced by chlorine. This replacement would not occur if either of the carbon atoms adjacent to the CH·OH group was fully substituted, in which circumstances elimination would be expected to occur, as with (XI) above. If the lanostane ring system (III) were present in polyporenic acid C, a possibility indicated earlier, then the only carbon atom in the five-membered ring D to which the hydroxyl group could be attached would be $C_{(16)}$ (cf. XVII).



(XVII)

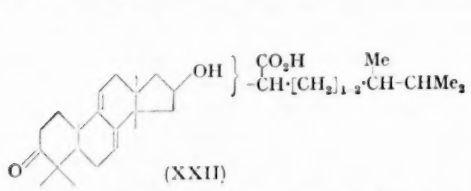
The keto-group in the chloro-compound (XVIII) was reduced with sodium borohydride and the resulting chloro-hydroxy-ester (XIX) was treated with lithium aluminium hydride to reduce the methoxycarbonyl group. Besides the expected chlorodihydroxy-compound (XX), a triol was obtained which was identical with the triol (XXI) resulting from the reduction of methyl dihydropolyporenate C with lithium aluminium hydride. The chlorine atom had thus been replaced by a hydroxyl group: a most unexpected result. One possible explanation appeared to be that the methoxycarbonyl group was in either the $\gamma$ or the $\delta$ position to the chlorine-substituted carbon atom, and that during the reduction a negative ion arising from the carboxyl group displaced the chlorine atom in an $S_N2$ reaction, and that the resulting intermediate was later hydrolysed. When the possibility of a steroid-type side chain in acid C was borne in mind this explanation suggested the sequence of reactions (IV ⟶ XXI), and the presence in polyporenic acid C of the partial grouping represented in (IV). The lithium aluminium hydride reduction will be discussed more fully in a later publication. When the work already described was complete it was possible to put forward a partial structure (XXII) for dihydropolyporenic acid C which was based on the lanostane ring system and included the groupings (XII) and (XVI), and the 5-membered ring system in (IV). An attractive complete structure was (XXIII) which has a $C_{31}$ formula and bears the same relation to the lanosterol carbon skeleton as that



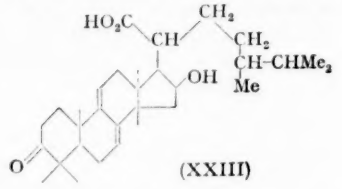

of ergostanol does to the cholestanol skeleton. This somewhat revolutionary $C_{31}$ possibility had been under consideration for some time for polyporenic acid A (cf. Cross, Eliot, Heilbron, and Jones, *J.*, **1940**, 632, and the comment on the formula of polyporenic acid A; Curtis, Heilbron, Jones, and Woods, *J.*, 1953, 457) although it suffered from the apparent disadvantage that it did not allow an isoprenoid structure. However, with the elucidation of the structure of lanosterol and the proof that it was a $C_{30}$ trimethyl-steroid, not obeying

the isoprene rule (cf. Voser, Mijovic, Heusser, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1952, **35**, 2414), this inhibition disappeared. In fact the existence of trimethyl-steroids with ergostanol and stigmastanol type side-chains appeared an attractive possibility.

At this stage, through the courtesy of Professor A. Robertson, F.R.S., Dr. J. S. E. Holker, and their colleagues at Liverpool, we learned that a relation had been established between

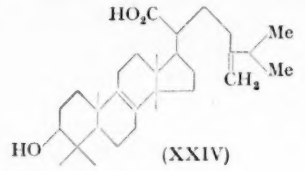



(XXII)

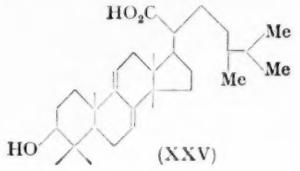



(XXIII)

lanosterol and eburicoic acid and that the latter had now been proved to be a $C_{31}$ compound with structure (XXIV) (Holker, Powell, Robertson, Simes, Wright, and Gascoigne, *J.*, 1953, 2422). It was apparent that if dihydropolyporenic acid C was (XXIII) it should be convertible into a compound derived from eburicoic acid, *e.g.*, the dehydrodihydro-acid (XXV). The sodium borohydride reduction product (X) of the ketone (VI) obtained by oxidising methyl dihydropolyporenate C was reduced by the Wolff–Kishner method. The product was methylated and acetylated and proved to be identical with methyl acetyl-

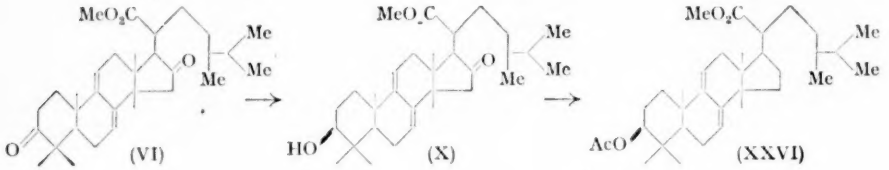



(XXIV)



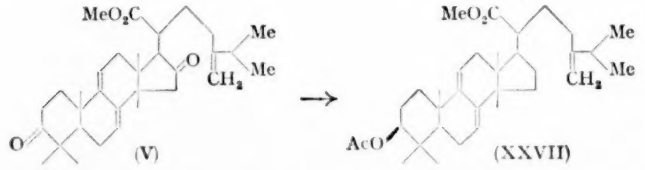

(XXV)

Methyl dihydropolyporenate C (XXIII)




Eburicoic acid (XXIV)

Methyl polyporenate C

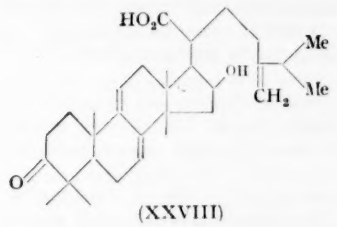



Eburicoic acid (XXIV)

dehydrodihydroeburicoate (XXVI) from eburicoic acid. A similar series of reactions starting from the sodium borohydride reduction product (IX) of the ketone (V) from methyl polyporenate C gave methyl acetyldehydroeburicoate (XXVII). Structure (XXIII) was thus confirmed for dihydropolyporenic acid C, and (XXVIII) followed for polyporenic acid C, the position of the vinylidene group being established by the conversion into methyl acetyldehydroeburicoate (XXVII).

On the assumption that no stereochemical inversion of the carbon atom carrying the carboxyl group occurs during the conversion into an eburicoic acid derivative the parent hydrocarbon of polyporenic acid C is eburicane (XXIX) (Holker *et al.*, *loc. cit.*), the stereochemistry of which is the same as that of lanostane (cf. Voser *et al.*, *loc. cit.*; Barnes, Barton, Fawcett, and Thomas, *J.*, 1953, 576). The systematic naming of polyporenic acid C derivatives described in this paper is based on eburicane which is numbered according to the rules of steroid nomenclature (*J.*, 1951, 3526) [there is no $C_{29}$ as this number is reserved for the additional carbon atom of the stigmastanol side chain (XXX)].

The evidence presented so far for the position (16) of the hydroxyl group in polyporenic acid C has depended on the phosphorus pentachloride reaction and on the interpretation of the lithium aluminium hydride reaction described above (XIX ⟶ XXI). This is supported by the molecular-rotation difference between the acetate of the 16-oxo-



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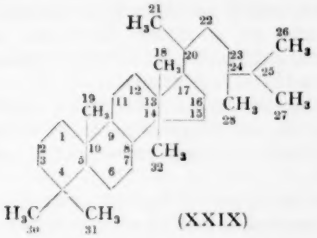
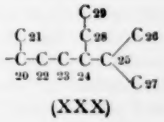
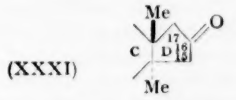


(XXIX)

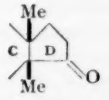


(XXX)

compound (X) and the corresponding deoxo-compound (XXVI). The value ($M_D$ −498°) is characteristic of the groupings (XXXI) and (XXXII) (Klyne, *J.*, 1952, 2916). Structure (XXXII) is additionally excluded, however, as it involves a C/D *cis*-fusion, while the C/D ring fusion in polyporenic acid C must be *trans*, as in lanosterol (XXXIII), as indicated by *X*-ray evidence (Curtis, Fridricksons, and Mathieson, *Nature*, 1952, **170**, 321) and by molecular-rotation data (Barnes, Barton, Fawcett, and Thomas, *loc. cit.*). Partial structure (XXXI) must therefore be present in the 16-oxo-compound (X).

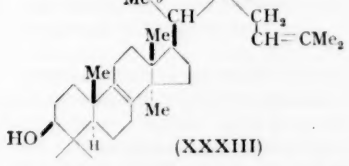


(XXXI)



(XXXII)

The infra-red spectra of the 16-oxo-compounds (IX) and (X) both exhibit a band at 1419 cm.$^{-1}$ in carbon tetrachloride. This is probably due to the bending vibration of the C–H bonds of the $C_{(15)}$ methylene group in the α-position to the carbonyl group. Jones and Cole (*J. Amer. Chem. Soc.*, 1952, **74**, 5648) list the positions of the bands due to the C–H bending vibration of $C_{(16)}$ methylene groups in a series of $C_{(17)}$ keto-steroids and conclude that they lie between 1404 and 1411 cm.$^{-1}$. Barton, Cole, *et al.* (*Chem. and Ind.*,



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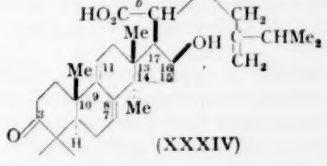

(XXXIV)

1952, 426) find that the analogous band of two 17-oxolanosterol derivatives also lies in this region. On the other hand, the infra-red spectrum of a carbon tetrachloride solution of kryptogenin acetate (kindly supplied by Dr. C. Djerassi), in which there is a $C_{(15)}$ methylene group in the α-position to a 16-oxo-group, as in derivatives of polyporenic acid C, exhibits no band between 1404 and 1411 cm.$^{-1}$. There is a band at 1418 cm.$^{-1}$ but it is not known whether this is due to the $C_{(15)}$ or the $C_{(23)}$ methylene group. These results suggest that it

may be possible to distinguish between 16- and 17-keto-steroids on the basis of infra-red data.

The 3-hydroxyl group formed on reduction of the oxo group of polyporenic acid C must have the β(equatorial)-configuration because of the course of the phosphorus pentachloride dehydration reaction.

The configuration of the $C_{(16)}$-hydroxyl group in polyporenic acid C is more difficult to determine and evidence concerning it is not yet complete. The reactions so far investigated, including the lithium aluminium hydride reduction of the chloro-compound (XIX), are best explained if the $C_{(16)}$-hydroxyl group is assumed to be β.

On the basis of the evidence presented polyporenic acid C is formulated as (XXXIV).

## Experimental

Rotations were determined in chloroform at room temperature unless otherwise stated. M. p.s were determined on a Kofler block and are corrected. The alumina used for chromatography had an activity I—II. Light petroleum refers to the fraction with b. p. 60—80°. Yields are of once crystallised material.

*Extraction of Polyporenic Acid C* (XXVIII; XXXIV) *from* Polyporus betulinus *Fr. and Isolation of the Methyl Ester.*—(Measurement of the light absorption at 2430 Å gave a useful indication of the amount of polyporenic acid C present at each stage of its extraction and purification.)

The residual fungus (4 kg.) after the extraction of polyporenic acid A (Curtis *et al., loc. cit.*) was reminced and suspended in boiling acetone for 16 hr. The solvent was decanted, and the last traces were removed by means of a basket centrifuge. Evaporation of the solvent from the combined solutions gave a greasy yellow solid (100 g.). Light absorption in ethanol: Max., 2430 Å; $\varepsilon = 4500$. This was suspended in ether (500 c.c.) and treated with an excess of diazomethane in ether. After several hours the excess of diazomethane was decomposed with acetic acid, and the ethereal solution filtered from an insoluble residue (10 g.). The residue obtained on removal of the ether was adsorbed from benzene (500 c.c.) on alumina (2 kg.). Elution with benzene–ether (9 : 1; 15 l.) gave a crude methyl ester (20 g.) which crystallised as needles, m. p. 175—190°, from methanol. Light absorption in ethanol: Max., 2430 Å; $\varepsilon = 14{,}500$.

Two methods have been adopted for purifying this crude methyl ester: (*a*) The crude methyl ester (8 g.) in ethanol (100 c.c.) containing acetic acid (10 c.c.) was refluxed with Girard's reagent T (7·5 g.) for 1 hr. The cooled mixture was poured into a solution of sodium carbonate (8·0 g.) in ice-water. Ether-extraction removed the non-ketonic material, and the residual aqueous solution was acidified with concentrated hydrochloric acid and kept at 20° for 1 hr. Ether-extraction and crystallisation from methanol gave *methyl polyporenate C* [*methyl* 16β-*hydroxy*-3-*oxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate*] as needles (4·6 g.), m. p. 191—195° raised by repeated crystallisation from methanol, ethanol, or aqueous acetone, to 198—199°, $[\alpha]_D$ +10° (*c*, 0·95) (Found: C, 77·0; H, 9·85. $C_{32}H_{48}O_4$ requires C, 77·35; H, 9·75%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; $\varepsilon = 14{,}600$, 16,900, and 11,200. Inflexion, 2760—2820 Å; $\varepsilon = 57$. The infra-red spectrum determined in carbon tetrachloride had bands at 891, 1639, 1712, 1738, and 3641 $cm.^{-1}$.

(*b*) The crude methyl ester (8 g.) was adsorbed from benzene (200 c.c.) on alumina (400 g.). Elution with benzene–ether (9 : 1; 6 l.) and crystallisation from methanol gave needles of methyl polyporenate C (5·5 g.), m. p. 192—196°, raised by repeated crystallisation to 198—199°.

*Isolation of Crude Polyporenic Acid C.*—The solid (1 g.) from the acetone extract of the fungus (see above) was adsorbed from benzene (50 c.c.) on alumina (80 g.) which had been deactivated by shaking a suspension in benzene with aqueous acetic acid (8 g.; 10%). Elution with benzene–ether (1 : 1; 200 c.c.) gave a fraction which separated from acetic acid as an amorphous solid (300 mg.), m. p. 245—252°. Light absorption in ethanol: Max., 2430 Å; $\varepsilon = 12{,}000$. Methylation of this acid with diazomethane, followed by chromatographic purification, gave methyl polyporenate C identical with an authentic sample.

*Hydrolysis of Methyl Polyporenate C.*—Methyl polyporenate C (3·0 g.) was heated under reflux for 16 hr. with methanolic potassium hydroxide (250 c.c.; 10%). After dilution with water (400 c.c.) and two extractions with ether to remove non-acidic material, acidification with acetic acid precipitated the crude acid (2·7 g.), m. p. 237—260°. A solution in ether–dioxan

(7 : 3; 1500 c.c.) was adsorbed on alumina (200 g.) which had been deactivated by shaking a suspension in ether with aqueous acetic acid (15 g.; 10%). Elution with ether–methanol (3 : 1; 4 l.) gave 16β-*hydroxy*-3-*oxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oic acid* (XXXIV) (1·4 g.), m. p. 273—276° (after repeated crystallisation from aqueous dioxan, acetic acid, or *iso*propanol), $[\alpha]_D$ +6° (*c*, 0·80 in pyridine) (Found: C, 76·6; H, 9·4. $C_{31}H_{46}O_4$ requires C, 77·1; H, 9·6%) (Found: equiv., 474, 468. $C_{33}H_{44}O_4$ requires equiv., 469. $C_{31}H_{46}O_4$ requires equiv., 483). Light absorption in ethanol: Max., 2360, 2430, and 2520 Å; ε = 14,550, 16,850, and 11,300.

Methylation of this acid with diazomethane followed by chromatographic purification gave methyl polyporenate C, m. p. 196—198°, undepressed on admixture with an authentic sample, $[\alpha]_D$ +10° (*c*, 1·31).

16β-*Acetoxy*-3-*oxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oic Acid*.—Polyporenic acid C (500 mg.) in pyridine (3 c.c.), treated with acetic anhydride (0·75 c.c.) at 20° for 16 hr., gave the 16-*acetate* as needles (420 mg.) (from aqueous acetic acid), m. p. 193—198°, raised by crystallisation from acetic acid or methanol to 206—210°, $[\alpha]_D$ −22° (*c*, 1·1) (Found: C, 75·5; H, 9·15. $C_{33}H_{48}O_5$ requires C, 75·55; H, 9·2%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; ε = 16,350, 18,900, and 12,400.

*Methyl* 16β-*Acetoxy*-3-*oxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate*.—Methyl polyporenate C (800 mg.) in pyridine (6 c.c.) was treated with acetic anhydride (3 c.c.) at 20° for 16 hr. Dilution with water and extraction with ether yielded a product which was adsorbed from light petroleum (50 c.c.) on alumina (80 g.). Elution with benzene (1 l.) gave the 16β-*acetoxy*-ester as needles (from methanol) (650 mg.), m. p. 122—124° (after repeated crystallisation from methanol or aqueous acetone), $[\alpha]_D$ −29° (*c*, 0·95) (Found: C, 75·45; H, 9·45. $C_{34}H_{50}O_5$ requires C, 75·8; H, 9·35%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; ε = 15,100, 17,800, and 11,800. Hydrolysis of the acetate (420 mg.) with methanolic potassium hydroxide (20 c.c.; 10%) at 20° for 16 hr. gave methyl polyporenate C (350 mg.), m. p. 196·5—198·5° (from methanol), undepressed on admixture with an authentic sample, and having $[\alpha]_D$ +11° (*c*, 0·95).

*Methyl Polyporenate C* 2 : 4-*Dinitrophenylhydrazone*.—Methyl polyporenate C (150 mg.) in ethanol (15 c.c.) was heated under reflux for ½ hr. with 2 : 4-dinitrophenylhydrazine (75 mg.) in ethanol (15 c.c.) containing a few drops of concentrated sulphuric acid. After dilution with water the derivative was isolated and adsorbed from benzene (25 c.c.) on alumina (15 g.). Elution with benzene gave the 2 : 4-*dinitrophenylhydrazone* which separated from ethanol–nitromethane as orange needles, m. p. 195—198°, $[\alpha]_D$ −69° (*c*, 1·00) (Found: C, 67·0; H, 7·95; N, 8·6. $C_{38}H_{52}O_7N_4$ requires C, 67·4; H, 7·75; N, 8·3%). Light absorption in ethanol: Max., 3660 Å; ε = 23,600.

*Methyl* 16β-*Hydroxy*-3-*oxoeburico*-7 : 9(11)-*dien*-21-*oate* (IV; XXIII).—Methyl polyporenate C (1·0 g.) in ethanol (75 c.c.) was hydrogenated for 45 min. at 20° in presence of Adams's catalyst (50 mg.) [uptake of $H_2$: 59 c.c. (N.T.P.). Calc. for 1 double bond: 55 c.c. (N.T.P.)]. After filtration and evaporation the product was adsorbed from benzene (50 c.c.) on alumina (100 g.). Elution with benzene–ether (7 : 3; 600 c.c.) gave *methyl* 16β-*hydroxy*-3-*oxoeburico*-7 : 9(11)-*dien*-21-*oate* as needles (900 mg.), m. p. 195—197° (after several crystallisations from acetone and methanol), $[\alpha]_D$ +10° (*c*, 1·12) (Found: C, 75·5; H, 10·0. $C_{32}H_{50}O_4,\frac{1}{2}CH_3{\cdot}OH$ requires C, 75·8; H, 10·2%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; ε = 14,750, 16,900, and 11,250. Inflexion, 2760—2820 Å; ε = 67. The infra-red spectrum determined in carbon tetrachloride had bands at 1714, 1738, and 3634 cm.$^{-1}$. The alcohol (450 mg.) in pyridine (20 c.c.) was treated with acetic anhydride (2·0 c.c.) at 20° for 16 hr. After dilution with water, isolation with ether gave the 16β-*acetoxy*-compound as needles (390 mg.), m. p. 131—137° (from methanol), raised by several crystallisations from methanol or aqueous ethanol to 139—141°, $[\alpha]_D$ −24° (*c*, 1·16) (Found: C, 75·7; H, 9·8. $C_{34}H_{52}O_5$ requires C, 75·5; H, 9·7%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; ε = 11,500, 13,150, and 8860.

*General Method of Oxidation with Chromic Acid*.—A cold solution of chromic acid (267 g.) in concentrated sulphuric acid (230 c.c.) and water (400 c.c.) was made up to 1 l. This solution is 8N with respect to oxygen. The compound to be oxidised was dissolved in pure acetone (distilled over potassium permanganate) at 20°, and the reagent added dropwise from a microburette until a persistent orange-brown coloration indicated that oxidation was complete.

*Methyl* 3 : 16-*Dioxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate* (V).—Methyl polyporenate C (500 mg.) was oxidised as described above. After 10 min. dilution with water and isolation with ether yielded a product which was adsorbed from light petroleum (50 c.c.) on alumina (50 g.). Elution with light petroleum–benzene (1 : 1; 800 c.c.) gave *methyl* 3 : 16-*dioxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate* as plates (350 mg.), m. p. 164·5—165·5° (after repeated crystallisation from methanol), $[\alpha]_D$ −68° (*c*, 1·00) (Found: C, 77·6; H, 9·4. $C_{32}H_{46}O_4$ requires C, 77·7;

H, 9·35%). Light absorption in ethanol: Max., 2360, 2430, and 2930 Å; $\varepsilon$ = 14,700, 16,600, and 71. Inflexion, 2510 Å; $\varepsilon$ = 11,000. The infra-red spectrum determined in Nujol had bands at 896, 1639, 1711, 1727, and 1743 cm.$^{-1}$. The *bis*-2 : 4-*dinitrophenylhydrazone* prepared in the usual way separated as needles, m. p. 233—236°, from methanol–nitromethane (Found: C, 62·0; H, 6·1; N, 13·45. $C_{44}H_{54}O_{10}N_8$ requires C, 61·8; H, 6·35; N, 13·1%). Light absorption in chloroform: Max., 3660 Å; $\varepsilon$ = 51,200.

*Methyl* 3 : 16-*Dioxoeburico*-7 : 9(11)-*dien*-21-*oate* (VI).—(*a*) Methyl 3 : 16-dioxoeburico-7 : 9(11) : 24(28)-trien-21-oate (210 mg.) in ethanol (50 c.c.) was hydrogenated in the usual way (uptake of $H_2$ after 35 min., 1·1 mol.). Removal of the catalyst and evaporation of the filtrate yielded a product which was adsorbed from light petroleum (20 c.c.) on alumina (20 g.). Elution with light petroleum–benzene (1 : 1; 500 c.c.) gave *methyl* 3 : 16-*dioxoeburico*-7 : 9(11)-*dien*-21-*oate* as needles (180 mg.) or plates, m. p. 166—168° (after several crystallisations from methanol), $[\alpha]_D$ −67° (*c*, 0·95) (Found: C, 76·95, 77·45; H, 9·8, 9·65. $C_{32}H_{48}O_4$ requires C, 77·35; H, 9·75%). Light absorption in ethanol: Max., 2360, 2430, and 2930 Å; $\varepsilon$ = 14,900, 16,600, and 86. Inflexion, 2510 Å; $\varepsilon$ = 11,150. The infra-red spectrum determined in Nujol had bands at 1712, 1729, and 1738 cm.$^{-1}$.

(*b*) Methyl dihydropolyporenate C (200 mg.) in acetone (50 c.c.) was oxidised with chromic acid as described above. Isolation with ether, purification by chromatography, and crystallisation as in (*a*), yielded the same ester, $[\alpha]_D$ −68° (*c*, 0·85), m. p. 167—169° alone or mixed with a specimen prepared as in (*a*). The infra-red spectrum was identical.

*Methyl* 3β : 16β-*Dihydroxyeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate* (VII).—Methyl polyporenate C (1·2 g.) in dioxan (50 c.c.) was treated with sodium borohydride (115 mg.) in aqueous dioxan (1 : 1; 15 c.c.) at 20° for 1 hr. Dilution with water and isolation with ether yielded a product which was adsorbed from benzene (100 c.c.) on alumina (120 g.). Elution with benzene–ether (4 : 1; 1300 c.c.) gave *methyl* 3β : 16β-*dihydroxyeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate* as needles (900 mg.), m. p. 177—179° (after several crystallisations from methanol), $[\alpha]_D$ +26° (*c*, 1·14) (Found: C, 74·4; H, 9·9. $C_{32}H_{50}O_4,CH_3{\cdot}OH$ requires C, 74·65; H, 10·25%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; $\varepsilon$ = 13,870, 16,400, and 10,970.

*Methyl* 3β : 16β-*Diacetoxyeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate*.—Methyl 3β : 16β-dihydroxyeburico-7 : 9(11) : 24(28)-trien-21-oate (200 mg.) in pyridine (3 c.c.) was treated with acetic anhydride (1 c.c.) at 20° for 16 hr. Dilution with water and isolation with ether yielded a product which was adsorbed from light petroleum (20 c.c.) on alumina (20 g.). Elution with light petroleum–benzene (1 : 1; 500 c.c.) and repeated crystallisation from methanol–nitromethane gave *methyl* 3β : 16β-*diacetoxyeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate* as needles, m. p. 110—114°, remelting at 145—147°, $[\alpha]_D$ +24° (*c*, 0·90) (Found: C, 73·15; H, 9·3. $C_{36}H_{54}O_6{\cdot}\frac{1}{2}CH_3{\cdot}OH$ requires C, 73·2; H, 9·45%). Light absorption in ethanol: Max., 2370, 2440, and 2520 Å; $\varepsilon$ = 14,100, 16,400, and 10,800.

*Oxidation of Methyl* 3β : 16β-*Dihydroxyeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate*.—Methyl 3β : 16β-dihydroxyeburico-7 : 9(11) : 24(28)-trien-21-oate (100 mg.) in acetone (20 c.c.) was oxidised with chromic acid as described above. Isolation with ether yielded a product which was adsorbed from light petroleum (10 c.c.) on alumina (10 g.). Elution with light petroleum–benzene (1 : 1; 150 c.c.) gave methyl 3 : 16-dioxoeburico-7 : 9(11) : 24(28)-trien-21-oate (73 mg.), m. p. 164—165° (after two crystallisations from methanol) undepressed on admixture with an authentic sample, $[\alpha]_D$ −68° (*c*, 0·79).

*Methyl* 3β : 16β-*Dihydroxyeburico*-7 : 9(11)-*dien*-21-*oate* (VIII).—(*a*) Methyl dihydropolyporenate C (200 mg.) in dioxan (35 c.c.) was treated with sodium borohydride (20 mg.) in aqueous dioxan (1 : 1; 10 c.c.) at 20° for 1 hr. Dilution with water and isolation with ether yielded a product which was adsorbed from benzene (20 c.c.) on alumina (20 g.). Elution with benzene–ether (6 : 1; 300 c.c.) gave *methyl* 3β : 16β-*dihydroxyeburico*-7 : 9(11)-*dien*-21-*oate* as needles (175 mg.), m. p. 188—190° (after several crystallisations from methanol), $[\alpha]_D$ +24° (*c*, 0·86) (Found: C, 74·05; H, 10·4. $C_{32}H_{52}O_4,CH_3{\cdot}OH$ requires C, 74·4; H, 10·6%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; $\varepsilon$ = 13,900, 16,300, and 11,000.

(*b*) Methyl 3β : 16β-dihydroxyeburico-7 : 9(11) : 24(28)-trien-21-oate (480 mg.) in glacial acetic acid (30 c.c.) was hydrogenated in the usual way [uptake of $H_2$ after 1·5 hr., 21 c.c. (N.T.P.). Calc. for one double bond: 22 c.c.]. Filtration and evaporation yielded a product which was adsorbed from benzene (50 c.c.) on alumina (50 g.). Elution with benzene–ether (6 : 1; 500 c.c.) gave methyl 3β : 16β-dihydroxyeburico-7 : 9(11)-dien-21-oate as needles (430 mg.), m. p. 188—190° (after repeated crystallisation from methanol or ethanol) undepressed on admixture with a specimen prepared as in (*a*), $[\alpha]_D$ +27° (*c*, 0·85).

*Methyl* 3 : 16-*Diacetoxyeburico*-7 : 9(11)-*dien*-21-*oate*.—Methyl 3 : 16-diacetoxyeburico-

7 : 9(11) : 24(28)-trien-21-oate (219 mg.) in ethanol (50 c.c.) was hydrogenated in the usual way. Filtration and evaporation yielded a product which was adsorbed from light petroleum–benzene (4 : 1; 20 c.c.) on alumina (20 g.). Elution with light petroleum–benzene (1 : 1; 500 c.c.) gave *methyl* 3 : 16-*diacetoxyeburico*-7 : 9(11)-*dien*-21-*oate* as needles (200 mg.), m. p. 169—171° (after several crystallisations from methanol), $[\alpha]_D$ +20° (*c*, 1·06) (Found: C, 74·05; H, 9·7. $C_{36}H_{56}O_6$ requires C, 73·95; H, 9·65%). Light absorption in ethanol: Max. 2360, 2430, and 2510 Å; $\varepsilon$ = 13,900, 16,100, and 10,600.

*Oxidation of Methyl* 3β : 16β-*Dihydroxyeburico*-7 : 9(11)-*dien*-21-*oate*.—Methyl 3β : 16β-dihydroxyeburico-7 : 9(11)-dien-21-oate (200 mg.) in acetone (50 c.c.) was oxidised with chromic acid as described above. Isolation with ether yielded a product which was adsorbed from light petroleum (20 c.c.) on alumina (20 g.). Elution with light petroleum–benzene (1 : 1; 500 c.c.) gave methyl 3 : 16-dioxoeburico-7 : 9(11)-dien-21-oate as needles (160 mg.), m. p. 165·5—167·5° (after repeated crystallisation from methanol and aqueous acetone) undepressed on admixture with an authentic sample. $[\alpha]_D$ −67° (*c*, 0·74). The infra-red spectrum was identical with that of an authentic sample.

*Methyl* 3β-*Hydroxy*-16-*oxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate* (IX).—Methyl 3 : 16-dioxoeburico-7 : 9(11) : 24(28)-trien-21-oate (480 mg.) in dioxan (30 c.c.) was treated with sodium borohydride (90 mg.) in aqueous dioxan (1 : 1; 30 c.c.) at 20° for 1 hr. Dilution with water and isolation with ether then yielded a product which was adsorbed from light petroleum (50 c.c.) on alumina (50 g.). Elution with benzene (900 c.c.) gave *methyl* 3β-*hydroxy*-16-*oxoeburico*-7 : 9(11)-24(28)-*trien*-21-*oate* as flat needles (330 mg.), m. p. 156—158° (after several crystallisations from aqueous methanol), $[\alpha]_D$ −52° (*c*, 1·00) (Found: C, 76·9; H, 9·75. $C_{32}H_{48}O_4$ requires C, 77·35; H, 9·75%). Light absorption in ethanol: Max., 2430 Å; $\varepsilon$ = 16,600. Inflexions, 2370, 2510, and 2890 Å; $\varepsilon$ = 15,100, 11,300, and 51. The infra-red spectrum determined in carbon tetrachloride had bands at 893, 1648, and 1743 cm.$^{-1}$. The 1743-cm.$^{-1}$ band was broad and due to two carbonyl groups, the methoxycarbonyl C=O group and the 5 membered-ring C=O group.

*Oxidation of Methyl* 3β-*Hydroxy*-16-*oxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate*.—Methyl 3β-hydroxy-16-oxoeburico-7 : 9(11) : 24(28)-trien-21-oate (70 mg.) in acetone (20 c.c.) was oxidised with chromic acid as described above. Isolation with ether yielded a product which was purified by chromatography on alumina, to give methyl 3 : 16-dioxoeburico-7 : 9(11) : 24(28)-trien-21-oate (50 mg.) as plates (from methanol), m. p. 164—165° undepressed on admixture of the sample with an authentic specimen, $[\alpha]_D$ −69° (*c*, 0·87). The infra-red spectrum was identical with that of an authentic sample.

*Methyl* 3β-*Acetoxy*-16-*oxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate*.—Methyl 3β-hydroxy-16-oxoeburico-7 : 9(11) : 24(28)-trien-21-oate (235 mg.) in pyridine (10 c.c.) was treated with acetic anhydride (1·5 c.c.) at 20° for 16 hr. Dilution with water and extraction with ether then yielded a product which was adsorbed from light petroleum (20 c.c.) on alumina (20 g.). Elution with benzene (400 c.c.) gave *methyl* 3β-*acetoxy*-16-*oxoeburico*-7 : 9(11) : 24(28)-*trien*-21-*oate* as needles (200 mg.), m. p. 186—188° (after repeated crystallisation from methanol), $[\alpha]_D$ −18° (*c*, 1·25) (Found: C, 75·35; H, 9·3. $C_{34}H_{50}O_5$ requires C, 75·8; H, 9·35%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; $\varepsilon$ = 13,400, 15,000, and 9900.

*Methyl* 3β-*Hydroxy*-16-*oxoeburico*-7 : 9(11)-*dien*-21-*oate* (X).—(*a*) Methyl 3β-hydroxy-16-oxoeburico-7 : 9(11) : 24(28)-trien-21-oate (315 mg.) in ethanol (50 c.c.) was hydrogenated in the usual way [uptake of $H_2$ after 1 hr., 19·5 c.c. (N.T.P.). Calc. for one double bond: 21 c.c.]. Filtration and evaporation yielded a product which was adsorbed from light petroleum (30 c.c.) on alumina (30 g.). Elution with benzene–ether (4 : 1; 600 c.c.) gave *methyl* 3β-*hydroxy*-16-*oxoeburico*-7 : 9(11)-*dien*-21-*oate* as plates (250 mg.), m. p. 174—177° (after repeated crystallisation from aqueous methanol), $[\alpha]_D$ −54° (*c*, 1·03) (Found: C, 77·05; H, 10·1. $C_{32}H_{50}O_4$ requires C, 77·05; H, 10·1%). Light absorption in ethanol: Max., 2430 Å; $\varepsilon$ = 16,800. Inflexions, 2360, 2510, and 2940 Å; $\varepsilon$ = 14,900, 11,300, and 35.

(*b*) Methyl 3 : 16-dioxoeburico-7 : 9(11)-dien-21-oate (300 mg.) in dioxan (40 c.c.) was treated with sodium borohydride (55 mg.) in aqueous dioxan (1 : 1, 15 c.c.) for 1 hr. at 20°. Dilution with water and isolation with ether then yielded a product which was adsorbed from benzene (30 c.c.) on alumina (30 g.). Elution with benzene–ether (4 : 1; 600 c.c.) gave methyl 3β-hydroxy-16-oxoeburico-7 : 9(11)-dien-21-oate as plates (225 mg.), m. p. 174—177° (after several crystallisations from aqueous methanol) undepressed on admixture with a specimen prepared as in (*a*), $[\alpha]_D$ −51° (*c*, 0·93). The infra-red spectrum was identical with that of a specimen prepared as in (*a*).

*Methyl* 3β-*Acetoxy*-16-*oxoeburico*-7 : 9(11)-*dien*-21-*oate*.—Methyl 3β-hydroxy-16-oxoburico-

7 : 9(11)-dien-21-oate (450 mg.) in pyridine (15 c.c.) was treated with acetic anhydride (3·0 c.c.) at 20° for 16 hr. After dilution with water, isolation with ether gave a product which was adsorbed from light petroleum (30 c.c.) on alumina (20 g.). Elution with light petroleum–benzene (1 : 1; 600 c.c.) gave the 3β-*acetate* as needles (400 mg.) (from methanol), m. p. 185—189° raised by several crystallisations from ethanol to 191—192°, $[\alpha]_D$ −24° (*c*, 1·18) (Found: C, 75·7; H, 9·6. $C_{34}H_{52}O_5$ requires C, 75·5; H, 9·7%).

*Ozonolysis of Methyl Polyporenate C.*—Methyl polyporenate C (540 mg.) in glacial acetic acid (20 c.c.) was treated with ozonised oxygen at 20° for 2 hr. Water was added and the mixture steam-distilled, the distillate being passed into a solution of dimedone (300 mg.) in aqueous ethanol (4 : 1; 10 c.c.). After 16 hr. at 0° the precipitate was collected, dried (143 mg.), and recrystallised from ethanol; it had m. p. 189—190°, undepressed on admixture with an authentic sample of the formaldehyde derivative, m. p. 189—190° (Found: C, 69·7; H, 8·25. Calc. for $C_{17}H_{24}O_4$: C, 69·8; H, 8·2%).

*Dehydration of Methyl* 3β-*Hydroxy*-16-*oxoeburico*-7 : 9(11)-*dien*-21-*oate.*—A suspension of methyl 3β-hydroxy-16-oxoeburico-7 : 9(11)-dien-21-oate (530 mg.) in light petroleum (50 c.c.) was shaken for 10 min. at 20° with phosphorus pentachloride (300 mg.). After addition to water, isolation with light petroleum gave a product which was adsorbed on alumina (30 g.) and eluted with light petroleum–benzene (1 : 1; 600 c.c.), to give a colourless oil (330 mg.) which has not yet crystallised.

*Ozonolysis of Phosphorus Pentachloride Dehydration Product.*—The dehydration product (230 mg.) in glacial acetic acid (20 c.c.) was treated with ozonised oxygen for 45 min. at 20°. Water was added and the mixture steam-distilled, the distillate being passed into a solution of dimedone (300 mg.) in methanol (15 c.c.). No precipitate resulted. The dimedone solution was in turn steam-distilled, the distillate being passed into a solution of 2 : 4-dinitrophenylhydrazine (300 mg.) in methanol (15 c.c.) containing a few drops of concentrated hydrochloric acid. Extraction of this solution with benzene gave a product which, after purification by chromatography, was crystallised from methanol and from ethanol to give acetone 2 : 4-dinitrophenylhydrazone (89 mg.) as plates, m. p. 124—125°, undepressed on admixture of the sample with an authentic specimen (Found: N, 23·75. Calc. for $C_9H_{10}O_4N_4$: N, 23·5%).

*Methyl* 16β-*Hydroxy*-3-*oxoeburico*-7 : 9(11) : 24(25)-*trien*-21-*oate* (XIII).—Hydrogen chloride was passed into a solution of methyl polyporenate C (911 mg.) in chloroform (250 c.c.) for 3 hr. at 20°. The solution was then poured on ice-water. Isolation with chloroform gave *methyl* 16β-*hydroxy*-3-*oxoeburico*-7 : 9(11) : 24(25)-*trien*-21-*oate* as needles (780 mg.), m. p. 174—177° (after several crystallisations from ethanol or aqueous acetone), $[\alpha]_D$ +3° (*c*, 1·19) (difficulty was experienced in the analysis of this compound. The least unsatisfactory analysis was: Found: C, 76·65; H, 9·65. $C_{32}H_{48}O_4$ requires C, 77·35; H, 9·75%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; ε = 13,000, 15,100, and 9950.

*Ozonolysis of Methyl* 16β-*Hydroxy*-3-*oxoeburico*-7 : 9(11) : 24(25)-*trien*-21-*oate.*—Methyl 16β-hydroxy-3-oxoeburico-7 : 9(11) : 24(25)-trien-21-oate (250 mg.) in ethyl acetate (30 c.c.) was treated with ozonised oxygen for 1 hr. at 20°. Ferrous sulphate solution was added (5%; 20 c.c.) and the mixture steam-distilled. Treated as above, the distillate gave no dimedone derivative but afforded acetone 2 : 4-dinitrophenylhydrazone as needles (103 mg.), m. p. and mixed 123—124° (Found: N, 23·55. Calc. for $C_9H_{10}O_4N_4$: N, 23·5%). The non-volatile product was isolated by ether-extraction and then shaken with aqueous sodium carbonate solution. No acid product could be isolated. Oxidation with excess of chromic acid in acetone in the usual way did not produce an acid product. The neutral product did not crystallise.

*Methyl* 16α-*Chloro*-3-*oxoeburico*-7 : 9(11)-*dien*-21-*oate* (XVIII).—A suspension of methyl 16β-hydroxy-3-oxoeburico-7 : 9(11)-dien-21-oate (500 mg.) in light petroleum (50 c.c.) was shaken with phosphorus pentachloride (350 mg.) at 20° for 10 min., the alcohol dissolving completely. Water was added and the product extracted with light petroleum. Removal of the solvent gave *methyl* 16α-*chloro*-3-*oxoeburico*-7 : 9(11)-*dien*-21-*oate* as needles (430 mg.), m. p. 176—178° (after repeated crystallisation from ethanol or acetone), $[\alpha]_D$ +35° (*c*, 2·50) (Found: C, 74·4; H, 9·6; Cl, 7·25. $C_{32}H_{49}O_3Cl$ requires C, 74·3; H, 9·55; Cl, 6·9%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; ε = 15,600, 17,800, and 11,900.

*Methyl* 16α-*Chloro*-3β-*hydroxyeburico*-7 : 9(11)-*dien*-21-*oate* (XIX).—Methyl 16α-chloro-3-oxoeburico-7 : 9(11)-dien-21-oate (330 mg.) in dioxan (50 c.c.) was treated with sodium borohydride (32 mg.) in aqueous dioxan (1 : 1, 10 c.c.) at 20° for 1 hr. After dilution with water, isolation with ether yielded a product which was adsorbed from benzene (50 c.c.) on alumina (30 g.). Elution with benzene–ether (7 : 3; 400 c.c.) gave *methyl* 16α-*chloro*-3β-*hydroxyeburico*-7 : 9(11)-*dien*-21-*oate* as needles (304 mg.), m. p. 209—210° (after repeated crystallisation from

methanol or ethanol), $[\alpha]_D$ +47° (*c*, 0·95) (Found: C, 73·7; H, 10·0; Cl, 6·85. $C_{39}H_{51}O_3Cl$ requires C, 74·0; H, 9·9; Cl, 6·85%). Light absorption in ethanol: Max.: 2360 and 2430 Å; $\varepsilon$ = 13,800 and 16,100. Inflexion, 2510 Å; $\varepsilon$ = 10,600.

*Methyl* 3β-*Acetoxy*-16α-*chloroeburico*-7 : 9(11)-*dien*-21-*oate*.—Methyl 16α-chloro-3β-hydroxyeburico-7 : 9(11)-dien-21-oate (160 mg.) in pyridine (10 c.c.) was treated with acetic anhydride (2 c.c.) at 20° for 48 hr. After dilution with water extraction with ether yielded a product which was adsorbed from light petroleum (20 c.c.) on alumina (15 g.). Elution with benzene (400 c.c.) gave *methyl* 3β-*acetoxy*-16α-*chloroeburico*-7 : 9(11)-*dien*-21-*oate* as plates (149 mg.), m. p. 184—187°, remelting at 191—193° (after several crystallisations from methanol), $[\alpha]_D$ +74° (*c*, 0·95) (Found: C, 72·25; H, 9·65; Cl, 6·6. $C_{34}H_{53}O_4Cl$ requires C, 72·75; H, 9·5; Cl, 6·3%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; $\varepsilon$ = 14,500, 17,000, and 11,200.

3β : 16β : 21-*Trihydroxyeburico*-7 : 9(11)-*diene* (XXI).—Methyl 3β : 16β-dihydroxyeburico-7 : 9(11)-dien-21-oate (228 mg.) in ether (100 c.c.) was heated under reflux for 1 hr. with lithium aluminium hydride (400 mg.). The excess of reagent was destroyed with ethyl acetate and the complex decomposed with 2N-hydrochloric acid (100 c.c.). Isolation with ether gave 3β : 16β : 21-*trihydroxyeburico*-7 : 9(11)-*diene* as needles or plates (200 mg.), m. p. 241—244° (after several crystallisations from ethanol or methanol), $[\alpha]_D$ +35° (*c*, 0·78 in pyridine) (Found: C, 79·1; H, 11·3. $C_{31}H_{52}O_3$ requires C, 78·75; H, 11·1%). Light absorption in ethanol: Max., 2370 and 2440 Å; $\varepsilon$ = 15,250 and 17,950. Inflexion, 2520 Å; $\varepsilon$ = 11,650.

This triol (150 mg.) in pyridine (10 c.c.) was treated with acetic anhydride (4 c.c.) at 20° for 72 hr. Dilution with water, extraction with ether, adsorption from benzene (15 c.c.) on alumina (15 g.), and elution with benzene (300 c.c.) gave the 3β : 16β : 21-*triacetate* as needles (136 mg.), m. p. 139—141° (after five crystallisations from methanol or ethanol), $[\alpha]_D$ +21° (*c*, 1·03) (Found: C, 73·85; H, 9·7. $C_{37}H_{58}O_6$ requires C, 74·2; H, 9·75%). Light absorption in ethanol: Max., 2360, 2430, and 2510 Å; $\varepsilon$ = 15,400, 18,000 and 11,900.

*Reduction of Methyl* 16α-*Chloro*-3β-*hydroxyeburico*-7 : 9(11)-*dien*-21-*oate with Lithium Aluminium Hydride*.—Methyl 16α-chloro-3β-hydroxyeburico-7 : 9(11)-dien-21-oate (320 mg.) in ether (125 c.c.) was treated with lithium aluminium hydride (400 mg.) at 20° for 48 hr. The excess of reagent was destroyed with ethyl acetate and the complex decomposed with 2N-hydrochloric acid (100 c.c.). Isolation with ether gave a product which was adsorbed from benzene (50 c.c.) on alumina (25 g.). Elution with benzene–ether (7 : 3; 600 c.c.) gave 16α-*chloro*-3β : 21-*dihydroxyeburico*-7 : 9(11)-*diene* (XX) as needles (190 mg.), m. p. 208—210° (after several crystallisations from methanol and ethanol), $[\alpha]_D$ +78° (*c*, 0·82) (Found: C, 75·1; H, 10·6; Cl, 7·15. $C_{31}H_{51}O_3Cl$ requires C, 75·75; H, 10·45; Cl, 7·2%). Light absorption in ethanol: Max.: 2370, 2440, and 2520 Å; $\varepsilon$ = 14,200, 16,600, and 10,050.

Elution with benzene–ether (1 : 1) gave 3β : 16β : 21-trihydroxyeburico-7 : 9(11)-diene as needles or plates (100 mg.) from ethanol, m. p. and mixed m. p. 241—244° (after crystallisation from ethanol), $[\alpha]_D$ +35° (*c*, 0·79 in pyridine). The infra-red spectrum was identical with that of an authentic sample.

The diol (176 mg.) in pyridine (10 c.c.) was treated with acetic anhydride (3 c.c.) at 20° for 72 hr. After dilution with water isolation with ether yielded a product which was adsorbed from light petroleum on alumina (15 g.). Elution with light petroleum–benzene (4 : 1; 500 c.c.) gave 3β : 21-*diacetoxy*-16α-*chloroeburico*-7 : 9(11)-*diene* as needles (155 mg.), m. p. 147—149° (after several crystallisations from methanol or ethanol), $[\alpha]_D$ +87° (*c*, 1·05) (Found: C, 73·1; H, 9·4. $C_{35}H_{55}O_4Cl$ requires C, 73·05; H, 9·6%). Light absorption in ethanol: Max., 2350, 2430, and 2520 Å; $\varepsilon$ = 13,800, 15,600, and 10,600.

*Methyl* 3β-*Acetoxyeburico*-7 : 9(11)-*dien*-21-*oate* (XXVI).—Methyl 3β-hydroxy-16-oxoeburico-7 : 9(11)-dien-21-oate (2·2 g.) in diethylene glycol (150 c.c.) was heated at 100° for 1½ hr. with hydrazine hydrate (5 c.c.; 90%); then the excess of hydrazine and water was removed by distillation. Potassium hydroxide (2 g.) was added and the solution heated under reflux for 5 hr. After acidification with acetic acid the cooled mixture was diluted with water, and the product was isolated with ether, suspended in acetone (150 c.c.), and treated with excess of ethereal diazomethane at 20° for 16 hr. The crude methyl ester was dissolved in pyridine (75 c.c.) and treated with acetic anhydride (3 c.c.) for 1½ hr. at 100°. Isolation with ether gave a product which was adsorbed from light petroleum–benzene (1 : 1) on alumina (150 g.). Elution with benzene (1800 c.c.) gave methyl 3β-acetoxyeburico-7 : 9(11)-dien-21-oate as needles (850 mg.) (from methanol), m. p. 163—166°, raised by several crystallisations from ethanol to 174—175°, undepressed on admixture with a sample of methyl acetyldehydrodihydroeburicoate; the product had $[\alpha]_D$ +70° (*c*, 0·96) (Found: C, 77·1; H, 10·4. Calc. for $C_{34}H_{54}O_4$: C, 77·5; H, 10·35%). The infra-red spectrum was identical with that of a sample of methyl acetyl-

dehydrodihydroeburicoate. Light absorption in ethanol: Max.: 2360, 2440, and 2520 Å; $\varepsilon$ = 15,900, 18,450, and 12,100.

*Methyl 3β-Acetoxyeburico-7 : 9(11) : 24(28)-trien-21-oate* (XXVII).—Methyl 3β-hydroxy-16-oxoeburico-7 : 9(11) : 24(28)-trien-21-oate (2·0 g.) in diethylene glycol (125 c.c.) was heated with hydrazine hydrate (5 c.c.; 90%), then with potassium hydroxide (6 hr.), and esterified and chromatographed, all as in the preceding experiment. Elution with benzene–ether (19 : 1; 1500 c.c.) gave methyl 3β-acetoxyeburico-7 : 9(11) : 24(28)-trien-21-oate as needles (790 mg.), m. p. and mixed m. p. 161—163° (after several crystallisations from methanol or ethanol), $[\alpha]_D$ +65° (*c*, 0·97) (Found: C, 77·55; H, 10·1. Calc. for $C_{34}H_{52}O_4$: C, 77·8; H, 10·0%). The infra-red spectrum was identical with that of methyl acetyldehydroeburicoate. Light absorption in ethanol: Max. 2360, 2430, and 2510 Å; $\varepsilon$ = 11,500, 13,900, and 9000.

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## 521. *The Ionisation of Guanidine and of Amino-acids in Sulphuric Acid.*

By GWYN WILLIAMS and MURIEL L. HARDY.

Cryoscopic *i*-factors in 99·9% sulphuric acid have been measured for three guanidine salts and for the corresponding sodium or ammonium salts. The results indicate that not more than 28% of the singly charged guanidinium cations accept a further proton in this medium. The guanidinium cation is therefore a very weak base, having $pK_a \sim -11$; and $\Delta pK$ for the two stages of ionisation of guanidine is unusually large, being of the order 25.

Measurements of *i*-factors for amino-acids in sulphuric acid closely confirm the results of O'Brien and Niemann (*J. Amer. Chem. Soc.*, 1951, **73**, 4264). The maximum proton uptake by the carboxyl group in glycine and α-alanine is 20%. It increases for amino-acids in which the amino- and carboxyl groups are more widely separated by methylene groups.

GUANIDINE is a very strong monoacid base, with $pK_a$ = 13·65 at 25° (Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469; Angyal and Warburton, *J.*, 1951, 2492); and many guanidine salts have been prepared, with both strong and weak acids (*e.g.*, by Marckwald and Struwe, *Ber.*, 1922, **55**, 457). The singly charged guanidinium cation still contains free amino-groups, but in none of the salts which have been isolated does guanidine behave as a diacid base. On the other hand, Hantzsch (*Ber.*, 1930, **63**, 1782) took the depression of freezing point of sulphuric acid by guanidine hydrogen carbonate (after subtraction of the depression caused by water formed in chemical reaction) to mean that the guanidine cation is triply charged in nearly anhydrous sulphuric acid, so that a proton is accepted (presumably) at each of the three nitrogen atoms in very acid conditions. However, Hantzsch's result is not free from ambiguity; for the dissolution of guanidine hydrogen carbonate is a complex process, and the cryoscopic constant which he used for sulphuric acid was not correct. Whether, or not, guanidine forms a multiply-charged cation in concentrated sulphuric acid is significant for its reactions in very acid media: for example, for its reversible reaction with nitric acid in sulphuric acid, to form nitroguanidine (Simkins and Williams, *J.*, 1952, 3086). Multiplication of charge on the cation would be expected to retard nitration and would help to account for the unfavourable equilibrium

constants observed in the most concentrated acids. New cryoscopic measurements with guanidine salts in sulphuric acid (Table 1) fail to support Hantzsch's conclusion for guanidine, and indicate, rather, that the singly-charged guanidinium cation is a very weak base.

The measurements are not claimed to be of the very highest precision (cf. Gillespie, Hughes, and Ingold, *J.*, 1950, 2473); but, where comparison is possible, the results agree with those obtained in the most accurate experiments (Gillespie, *ibid.*, pp. 2537, 2542). In order to eliminate idiosyncracy of apparatus or method, each of three guanidine salts has been paired with a sodium or ammonium salt having the same anion. The comparison salts are of known behaviour in sulphuric acid (Gillespie, *loc. cit.*): sodium benzoate should give an *i*-factor of 4 owing to formation of benzoic acid and then of its conjugate acid; and the benzenesulphonate and perchlorate, which form acids, too strong to take up a further proton, should give *i*-factors of 3. The reasons for minor deviations from these figures have been discussed by Gillespie (*loc. cit.*).

Each guanidine salt (Table 1) gives an *i*-factor only slightly higher than that of the uni-univalent comparison salt, instead of giving the *i*-factors of 5 for the benzoate and 4 for the two other salts which would be observed if the guanidine molecule took up two protons quantitatively in sulphuric acid. *i*-Factors of 6 and 5, corresponding to a triply charged guanidine cation, are out of the question.

TABLE 1. *i-Factors in sulphuric acid.*

| Anion | Cation | Comparison salt *i*-Factor | *i* (mean) | Guanidine salt *i*-Factor | *i* (mean) |
|---|---|---|---|---|---|
| Benzoate ..... | Na | 3·98, 3·98, 4·08, 4·06, 4·07, 4·03 | 4·03 | (4·16), 4·27, 4·28, 4·32, 4·23, 4·28 | 4·28 |
| Benzenesulphonate | Na | 3·16, 3·15, 3·21, 3·11, 3·14 | 3·15 (3·13) * | 3·39, 3·43, 3·48, 3·50, 3·41, 3·46, 3·44 | 3·44 |
| Perchlorate ..... | $NH_4$ | 2·92, 2·91, (2·85), 2·92, 2·94 | 2·92 (2·93) * | 3·28, 3·25, 3·21, 3·19, 3·24, 3·20 | 3·23 |

* *v*-Factors, Gillespie (*locc. cit.*).

*The Basic Ionisation Constant of the Guanidinium Cation.*—If the mean difference of 0·28 between the *i*-factors of the guanidine salts and the comparison salts can be taken to mean that the singly charged guanidinium cation is about 28% ionised to the doubly charged cation in 99·9% sulphuric acid, then the guanidinium cation is a weaker base than 2 : 4 : 6-trinitroaniline, which is about 61% ionised in the same medium and has $pK_a = -9{\cdot}29$ (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721; Hammett and Paul, *ibid.*, 1934, **56**, 827). In principle, the ionisation constant,* $pK_a^{I}$, might be derived (Hammett *et al.*, *locc. cit.*) from the equations

$$pK_a^{I} = -\log (a_{H^+} a_{GH^+}/a_{GH_2^{2+}}) = H_+ + \log \{[GH_2^{2+}]/[GH^+]\} \quad . \quad . \quad (1)$$

in which G stands for the neutral guanidine molecule. If $H_0 = -10{\cdot}5$ for 99·9% sulphuric acid is substituted in (1) for the unknown value of $H_+$, then with $[GH_2^{2+}]/[GH^+] = 0{\cdot}39$, $pK_a^{I} \sim -10{\cdot}9$. With certain assumptions, Brand, Horning, and Thornley (*J.*, 1952, 1374) have estimated that $H_+ \simeq H_0 - 0{\cdot}28$ for 100% sulphuric acid. With $H_+ \simeq -10{\cdot}8$, $pK_a^{I} \simeq -11{\cdot}2$. These results for $pK_a^{I}$ for guanidine can be no more than estimates of order of magnitude, for both the ionisation ratio and the value of the acidity function (very sensitive to change of medium composition in this region) are approximate; but even the rough estimate implies a prodigious stretch between the first and second ionisation constants for guanidine (Table 3).

*The Behaviour of Amino-acids.*—A similar influence of an existing positive charge upon basic ionisation in sulphuric acid occurs with amino-acids. By analogy with acetic acid (Hantzsch, *Z. physikal. Chem.*, 1907, **61**, 257), these might be expected to take up a proton at the carboxyl group, when dissolved in sulphuric acid. We had made preliminary

* Since the constant $pK_a$ refers, strictly, to the ionisation of the conjugate acid of a base, it seems logical to use the symbols $pK_a^{II}$ and $pK_a^{I}$, respectively, for *acceptance* of the first and second protons by a base.

In the text, the symbol $\Delta pK_1^{II}$ stands for $pK_a^{II} - pK_a^{I}$.

measurements of *i*-factors for amino-acids when the results of similar experiments were published by O'Brien and Niemann (*J. Amer. Chem. Soc.*, 1951, **73**, 4264). Our results are given, without further detail, in Table 2, since they agree closely with those of O'Brien and Niemann, shown in parentheses in the Table.

TABLE 2. *i-Factors for amino-acids,* $H_3\overset{+}{N}\cdot[CHR]_n\cdot CO_2H$, *in sulphuric acid.*

| R | H | Me | H | H | H |
|---|---|---|---|---|---|
| *n* | 1 | 1 | 2 | 3 | 5 |
| *i* | 2·2 (2·2) | 2·2 | 2·7 (2·7) | (2·9) | 3·0 (3·0) |

The existing positive charge almost inhibits proton uptake at the carboxyl group in glycine and α-alanine. If 20% proton uptake occurs with glycine (as supposed by O'Brien and Niemann), $pK_a^I$ from a similar equation to (1) is −11·1.

*First and Second Ionisation Constants of Bases.*—For ethylenediamine, $\Delta pK_I^{II} = 3{\cdot}0$ (Schwarzenbach, *Helv. Chim. Acta*, 1933, **16**, 522). For adjacent amino-groups, it has been estimated (*idem, ibid.*, 1936, **19**, 178) that in hydrazine $\Delta pK_I^{II} \simeq 9$. It seems surprising, therefore, that the residual amino-groups in the guanidinium cation are so weakly basic. On the other hand, it has already been noted (Flexser, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103) that when a base accepts a second proton only in very strong acid $\Delta pK_I^{II}$ may be large. Figures are given in Table 3. Comparison of p$K$ values determined in water with those based on measurements in sulphuric acid is significant, since the latter are calculated by means of the acidity function, $H_0$, and are thus referred to a standard state in water.

TABLE 3. *First and second ionisation constants of bases.*

| Base | $Ph\cdot CO_2^-$ | $Ph\cdot CO_2H$ | $CH_2(NH_3^+)\cdot CO_2^-$ | $CH_2(NH_3^+)\cdot CO_2H$ | $(NH_2)_2C{:}NH$ | $(NH_2)_2C{:}NH_2^+$ |
|---|---|---|---|---|---|---|
| $pK_a$ | 4·16 * | −7·26 * | 2·34 † | ~ −11·1 | 13·65 | ~ −10·9 |
| $pK_a^{II} - pK_a^I$ | 11·4 | | ~13·4 | | ~24·6 | |

* Flexser, Hammett, and Dingwall (*loc. cit.*).
† Cohn and Edsall, "Proteins, Amino Acids and Peptides," Reinhold, New York, 1943, p. 84.

Structural influences upon ionisation in guanidine are large. Thus, although guanidine itself is such a strong base, nitroguanidine is so weak that its salts are almost completely hydrolysed in water (Thiele, *Annalen*, 1892, **70**, 1). Wood (*J.*, 1903, **83**, 568) estimated the extent of hydrolysis by a catalytic method and obtained a (rough) figure corresponding to $pK_a \sim -0{\cdot}2$ for nitroguanidine. Instead of $\Delta pK_a \sim 2$ for the pair aniline and *m*-nitroaniline, introduction of the nitro-group into guanidine causes $\Delta pK_a \sim 14$. Lack of the special resonance stabilisation present in the guanidinium cation (estimated by Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1939, p. 198, as about 7 kcal./mole, corresponding to $\Delta pK \sim 5$) no doubt contributes to the relative weakness of nitroguanidine as a base, in comparison with guanidine. The same factor must oppose acceptance of a further proton by the guanidinium cation.

Electrostatic effects may also be considerable in the planar, symmetrical guanidinium cation, in which the C–N distance is 1·18 Å (Theilacker, *Z. Krist.*, 1931, **76**, 303; 1935, **90**, 51, 256). Bjerrum's original treatment of the first and second ionisations of dibasic acids (*Z. physikal. Chem.*, 1923, **106**, 219; cf. Greenspan, *Chem. Reviews*, 1933, **12**, 339) is not adequate when a charge is very near the centre of ionisation, but if Kirkwood and Westheimer's more elaborate theory (*J. Chem. Phys.*, 1938, **6**, 506; 1939, **7**, 437) is applied to the process $GH_2^{2+} + G \rightleftharpoons 2GH^+$, their expression for a spherical cavity (having low dielectric constant, but situated in a medium with the dielectric constant of water) of radius 2·65 Å (calculated from a Traube partial molar volume of 67 c.c. for guanidine; cf. Partington, "Physical Chemistry," Vol. II, Longmans, London, 1951, p. 24), containing unit positive charge at 1·18 Å from the centre, leads to $\Delta pK_I^{II} \sim 19{\cdot}5$. This amounts to omission of the N–H distance in locating the charge within the cavity [cf. Brand, Horning, and Thornley's treatment (*loc. cit.*) of the basic ionisation of the nitro-group]. If the distance from the centre of the cavity to the ionisable hydrogen atoms of the $NH_3^+$ group is to be taken into account (Westheimer and Shookhof, *J. Amer. Chem. Soc.*, 1939, **61**, 555),

then a large value ($\Delta pK_1^{II} \sim 13$) is obtainable only if the guanidinium cation is supposed to occupy a spherical cavity of radius about 4 Å. These calculations show only that a large electrostatic contribution to the value of $\Delta pK_1^{II}$ is not impossible if a charge is near enough to the centre of ionisation. The fact that the ion $GH_2^{2+}$ is not a symmetrical dibasic acid has been neglected, except for the omission of any statistical factor.

## Experimental

*Materials.*—Guanidine benzenesulphonate, m. p. 209—210° (Found: C, 39·2; H, 5·4; N, 19·3; S, 14·3. Calc. for $C_7H_{11}O_3N_3S$: C, 38·7; H, 5·1; N, 19·3; S, 14·8%), was made from guanidine carbonate and benzenesulphonyl chloride (Clarke and Gillespie, *J. Amer. Chem. Soc.*, 1932, **54**, 1966). Guanidine benzoate, m. p. 226—227° (Found: C, 53·3; H, 6·1; N, 23·2. Calc. for $C_8H_{11}O_2N_3$: C, 53·0; H, 6·1; N, 23·2%), was made from the carbonate and sodium benzoate (Walker, *J.*, 1949, 1996). Guanidine perchlorate, m. p. 247·5—248·5° (Found: C, 7·9; H, 3·9; N, 26·8; Cl, 22·2. Calc. for $CH_6O_4N_3Cl$: C, 7·5; H, 3·8; N, 26·3; Cl, 22·2%), was made by neutralising an aqueous solution of the carbonate with perchloric acid (Marckwald and Struwe, *loc. cit.*; Mazzucchelli and Rossi, *Gazzetta*, 1927, **57**, 383; cf. Glasner and Makovky, *J.*, 1953, 182).

The sodium or ammonium salts were purified and dried before use. The amino-acids (cf. Table 2) were commercial specimens.

The sulphuric acid was prepared by diluting redistilled oleum with 98% sulphuric acid to an acid of f. p. approx. 9·9°.

*Measurements.*—The cryoscopic cell was made entirely of glass except for a rubber collar holding a Beckmann thermometer in a close-fitting neck, and was essentially similar to that of Newman, Kuivila, and Garrett (*J. Amer. Chem. Soc.*, 1945, **67**, 704). It had a hand- or motor-operated stirrer with mercury seal. The cell was surrounded by an air-jacket with upward sloping side-arm and the whole was supported in a Dewar vessel.

Before a measurement, the cell was cooled in ice–salt and was then transferred to a similar Dewar vessel containing water at a temperature 2° below the freezing point to be measured. A supercooling of about 1·5° was permitted and was corrected for by the formula of Gillespie, Hughes, and Ingold (*loc. cit.*). F. p.s, read on the Beckmann mercury thermometer, were reproducible to within 0·005°, and did not change appreciably with time. For example, a sample of sulphuric acid solvent had f. p. (Beckmann reading) 1·405°, 1·403°, and 1·406° at times zero, 1 hr., and 7 hr. respectively; and a solution of sodium benzoate in sulphuric acid had f. p. 3·053°, 3·054° at zero time and 3·050° after 20 hr. in the apparatus.

*i*-Factors were calculated from the expression $ik = \Delta\theta/\Delta m$ where $\Delta\theta$ is the depression in the f. p. caused by a change $\Delta m$ in the molality of the solute; and $k$, the cryoscopic constant of sulphuric acid, is 5·98 deg. mole$^{-1}$ kg. (*idem, ibid.*). Only experiments in which $0{\cdot}5° < \Delta\theta < 1{\cdot}55°$ were included in the mean *i*-factors in Table 1. The accuracy of the results did not warrant the application of the corrections used for the calculation of υ-factors (*idem, ibid.*).

The results for one pair of salts are given in full.

| Ammonium perchlorate | | | Guanidinium perchlorate | | |
|---|---|---|---|---|---|
| $\Delta m$ | $\Delta\theta$ | $i$ | $\Delta m$ | $\Delta\theta$ | $i$ |
| 0·04388 | 0·765° | 2·92 | 0·04449 | 0·873° | 3·28 |
| 0·07980 | 1·388 | 2·91 | 0·06256 | 1·217 | 3·25 |
| 0·1086 | 1·881 | 2·90 | 0·08019 | 1·541 | 3·21 |
| 0·03632 | 0·620° | 2·85 | 0·0411 | 0·785° | 3·19 |
| 0·06067 | 1·061 | 2·92 | 0·05507 | 1·067 | 3·24 |
| 0·08082 | 1·425 | 2·94 | 0·07901 | 1·511 | 3·20 |

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## 522. *The β-Phenylserine Series. Part II.**

By Ernst D. Bergmann, H. Bendas, and Ch. Resnick.

The extent to which the synthesis of substituted phenylserine alkyl esters from glycine alkyl esters and aromatic aldehydes is applicable has been studied. Azeotropic condensation of the two reactants leads to the *erythro*-configuration, but use of an excess of the glycine ester gives the *threo*-compounds which correspond configurationally to chloramphenicol. 1-Carbethoxymethylpyridinium bromide forms, analogously, aldol condensation products (I) with aromatic aldehydes.

The two *N*-(*p*-nitrobenzylidene)-*p*-nitrophenylserine esters give, upon acetylation, the two ethyl 3-acetyl-2 : 5-di-*p*-nitrophenyloxazolidine-4-carboxylates (II).

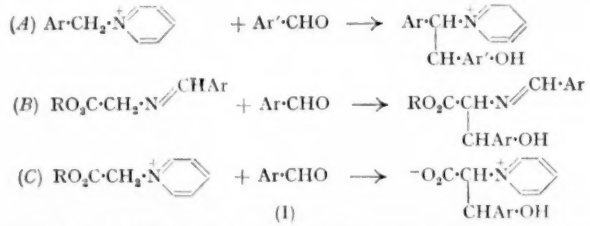
The ethyl esters of *O*-benzylserine and sarcosine condense with *p*-nitrobenzaldehyde under the influence of sunlight, to give ethyl α-amino-α-benzyloxymethyl-β-hydroxy-β-*p*-nitrophenylpropionate (IV) and ethyl 3-methyl-2 : 5-di-*p*-nitrophenyloxazolidine-4-carboxylate (VII), respectively.

The infra-red spectra of a number of the new compounds have been measured.

In Part I of this series * (cf. E. Bergmann, Bendas, and Genas, *Compt. rend.*, 1950, **231**, 361) the observation was recorded that certain aromatic aldehydes condense with glycine alkyl esters in alcohol with unexpected ease, to give Schiff bases derived from β-phenylserine, *viz.*, $Ar{\cdot}CH(OH){\cdot}CH(CO_2R){\cdot}N{:}CHAr$. The condensation product, m. p. 148°, of glycine ethyl ester with *p*-nitrobenzaldehyde appears to have been obtained by Gerngross and Zuehlke (*Ber.*, 1924, **57**, 1482), who however interpreted its structure incorrectly (see Holland and Nayler, *Chem. and Ind.*, 1952, 518). Hydrolysis of this Schiff base with hydrochloric acid gives the hydrochloride of *p*-nitrophenylserine ethyl ester, $NO_2{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH(NH_2){\cdot}CO_2Et$, m. p. 188° (decomp.).

Glycine benzyl ester reacts like the aliphatic esters of glycine.

It has been assumed that the first step of the synthesis is the formation of the Schiff base, $Ar{\cdot}CH{:}N{\cdot}CH_2{\cdot}CO_2R$, and the second the aldolisation reaction. Indeed, the reaction of *p*-nitrobenzaldehyde with glycine ethyl ester in ether can be interrupted at the stage of the Schiff base (*N*-*p*-nitrobenzylideneglycine ethyl ester), m. p. 86—87°, as already pointed out by Holland and Nayler (*loc. cit.*). This product has been obtained before by Dalgliesh (*J.*, 1949, 90) and by Billet and Marnay (*Compt. rend.*, 1951, **233**, 961), but has been erroneously assumed to be an isomer of *N*-(*p*-nitrobenzylidene)-*p*-nitrophenylserine ethyl ester, m. p. 148°.



The somewhat surprising aldolisation reaction (*B*) is analogous to the condensation (*A*) of 1-benzylpyridinium (and 1-allylpyridinium) salts with aromatic aldehydes, the methylene group, in both cases, being activated by the adjacent C:N double bond (Kroehnke and Vogt, *Ber.*, 1952, **85**, 368, and previous papers). Also the regularities governing the reactivity of the aromatic aldehydes are roughly the same in both cases: chlorine atoms and nitro-groups (the latter also in *m*-position to the aldehyde group) increase, and methoxyl and amino-groups decrease, the activity of the aldehyde group. The analogy is still more evident if one compares reaction (*B*) with that (*C*) of 1-carbethoxymethylpyridinium

* Part I, *J.*, 1951, 2673.

bromide. The latter compound condenses easily with *p*-nitro-, *p*-chloro-, and *o*-chlorobenzaldehyde in presence of one mol. of alkali. The analogous 1-*N'*-phenylcarbamylmethylpyridinium bromide responds in the same manner to *m*-nitrobenzaldehyde (Kroehnke and Vogt, *loc. cit.*). Also hydantoins and quinaldine are capable of giving aldol-type condensation products with "reactive" aromatic aldehydes (Phillips and Murphy, *J. Org. Chem.*, 1951, **16**, 954; Bahner and Pace, *J. Amer. Chem. Soc.*, 1952, **74**, 3932).

To the list of aldehydes which condense with glycine alkyl esters in the manner indicated (see Part I), there have been added 4-methyl-3-nitrobenzaldehyde and 5-nitrofurfuraldehyde. From the former, 4-methyl-3-nitrophenylserine methyl ester hydrochloride, and from the latter β-(5-nitro-2-furyl)serine ethyl ester hydrochloride and *N*-(5-nitro-2-furfurylidene)-β-(5-nitro-2-furyl)serine ethyl ester have been prepared (β-2-furylserine ethyl ester has been synthetised by Hayes and Gever, *J. Org. Chem.*, 1951, **16**, 269).

It had been tentatively assumed by Bergmann, Bendas, and Taub (*loc. cit.*) that the *p*-nitrophenylserine ethyl ester formed had the same configuration (*threo*) as Erlenmeyer's phenylserine, obtained from benzaldehyde and glycine in presence of concentrated aqueous alkali (see Part I, *loc. cit.*; Vogler, *Helv. Chim. Acta*, 1950, **33**, 2111; Billet, *Compt. rend.*, 1950, **230**, 1074; Alberti, Asero, Camerino, Sannicolo, and Vercellone, *Chim. e Ind.*, 1949, **31**, 357), and chloramphenicol. This assumption had been based on the observation that the lithium aluminium hydride reduction product of the ester showed some chloramphenicol activity. Close investigation has shown, however, that, mainly owing to an unexpected configurational instability of the *p*-nitrophenylserine system, the situation is much more complex. It can be summarised as follows :

(*a*) Whilst nitration of *threo*-β-phenylserine has so far given only ill-defined preparations of *threo*-*p*-nitrophenylserine (Billet, *Compt. rend.*, 1950, **230**, 1358; Woolley, *J. Biol. Chem.*, 1950, **185**, 293; Molho and Molho-Lacroix, *Compt. rend.*, 1951, **233**, 1067), *N*-dichloroacetylation, subsequent *O*-acetylation, and nitration of *threo*-phenylserine ethyl ester gives an *O*-acetyl-*N*-dichloroacetyl-*p*-nitrophenylserine ethyl ester (m. p. 127—128°), which undoubtedly has also the *threo*-configuration (Moersch, Rebstock, Moore, and Hylander, *J. Amer. Chem. Soc.*, 1952, **74**, 565). Equally, it has been shown by Feitelson, Gunner, Moualim, Petrow, Stephenson, and Underhill (*J. Pharm. Pharmacol.*, 1951, **3**, 149) and Kopp, Larramona, and Webuart (*Compt. rend.*, 1951, **233**, 527) that nitration of *threo-ON*-diacetylphenylserine ethyl ester leads to a *p*-nitro-ester of m. p. 120°. Alberti, Camerino, and Vercellone (*Experientia*, 1952, **8**, 261) moreover have obtained, by direct nitration of *threo*-phenylserine ethyl ester, *threo*-*p*-nitrophenylserine ethyl ester of m. p. 115·5—116° [hydrochloride, m. p. 153—155° (dec.)] (Holland and Jenkins, *Chem. and Ind.*, 1951, 1092). The following Table shows that the product obtained by direct condensation of *p*-nitrobenzaldehyde and glycine ethyl ester is different from *threo*-*p*-nitrophenylserine ethyl ester and must, therefore, be the *erythro*-compound. It may be assumed that all condensation products of glycine alkyl esters and aromatic aldehydes formed under the same conditions have the *erythro*-configuration.

(*b*) When *p*-nitrobenzaldehyde and glycine ethyl ester react in ethanolic or methanolic solution, the main crystalline product is the *erythro-N*-(*p*-nitrobenzylidene)-*p*-nitrophenylserine ethyl ester or *erythro-p*-nitrophenylserine ethyl ester hydrochloride, according to the method of working up. At the same time, small quantities of the *threo*-derivatives are formed; this is why in our first experiments the reduction of the crude—obviously sterically impure—ester with lithium aluminium hydride gave a product exhibiting chloramphenicol activity. That (*threo*)-*p*-nitrophenylserine can, indeed, be thus reduced to chloramphenicol has been proved by Huebner and Scholz (*J. Amer. Chem. Soc.*, 1951, **73**, 2089) and by Elphimoff-Felkin, Felkin, and Welvart (*Compt. rend.*, 1952, **234**, 1789; see Elphimoff-Felkin, Tchoubar, and Welvart, *Bull. Soc. chim.*, 1952, **19**, 252).

(*c*) The condensation of aromatic aldehydes and glycine alkyl esters can also be carried out by azeotropic condensation in presence of boiling benzene. Treatment of the crude products with hydrochloric acid gives the ester hydrochlorides of substituted β-phenylserines. In the cases studied (*p*- and *m*-nitro-, 2 : 6-dichloro-, and 4-methyl-3-nitrobenzaldehyde, and 5-nitrofurfuraldehyde), the products have been shown to possess the

*erythro*-configuration. In the azeotropic reaction between glycine methyl ester and *p*-chlorobenzaldehyde, the product appears to be *N*: α-di-*p*-chlorobenzylideneglycine methyl ester (see Experimental section).

*M. p.s of* threo- *and* erythro-p-*nitrophenylserine derivatives.*

| | *threo*-Series | *erythro*-Series |
|---|---|---|
| *p*-Nitrophenylserine | 188° [d]; 180—181° [e] | 187—188° [e] |
| *N*-Acetyl-*p*-nitrophenylserine | 191—192° [g] | 170° [e] |
| *p*-Nitrophenylserine Et ester | 115·5—116 [a, b]; 132 [i, m]; 147 [n]; 129—130° [o]; 133—134 [p] | 100—103 [b]; 112—113 [c, k]; 115—116 [i, m, n]; 114—115° [o] |
| *p*-Nitrophenylserine Et ester hydrochloride | 153—155 (dec.) [b]; 157—159 (dec.) [c] | 189 (dec.) [k]; 182—184 [b]; 176—179 (dec.) [c] |
| *N*-Dichloroacetyl-*p*-nitrophenylserine Et ester | 145 [a, d]; 177—178; 181—183 [e, f] | 131—132 [b, d] |
| *ON*-Diacetyl-*p*-nitrophenylserine Et ester | 122—124 [c]; 120 [d] | 138—139·5 [b, d, k] |
| *O*-Acetyl-*N*-dichloroacetyl-*p*-nitrophenylserine Et ester | 127—128 [d, f, g, l] | 86—87·5 [b, d] |
| *N*-(*p*-Nitrobenzylidene)-*p*-nitrophenylserine Et ester | 121—121·5 [a, f]; 120 [d] | 146—147 [e]; 148 [k] |
| *N*-Acetyl-*p*-nitrophenylserine Et ester | 182—184 [e] | 148—149 [e] |

[a] Feitelson *et al.*, *loc. cit.*; [b] Alberti, Camerino, and Vercellone, *loc. cit.*; [c] Alberti *et al.*, *loc. cit.*; [d] Present authors; [e] Carrara *et al.*, *Gazzetta*, 1950, **80**, 709; [f] We could not confirm this high m. p.; [g] Huebner and Scholz (*J. Amer. Chem. Soc.*, 1951, **73**, 2089) describe a hemihydrate of this compound of m. p. 108—109°. [h] E. Bergmann, Bendas, and Taub, *loc. cit.*; [i] Holland and Nayler, *loc. cit*; [k] Kopp *et al.*, *loc. cit.*; [l] Moersch *et al.*, *loc. cit.*; [m] Carrara, Pace, and Cristiani, *J. Amer. Chem. Soc.*, 1952, **54**, 4949; [n] Elphimoff-Felkin, Felkin, and Welvart, *Compt. rend.*, 1952, **235**, 1510; [o] Holland, Jenkins, and Nayler, *J.*, 1953, 273; [p] Elphimoff-Felkin, Felkin, and Welvart, *Compt. rend.*, 1952, **234**, 1627.

(*d*) The Schiff base, initially formed from glycine ethyl ester and *p*-nitrobenzaldehyde (see above), when kept in presence of alcohol, is gradually transformed into *erythro-N*-(*p*-nitrobenzylidene)-*p*-nitrophenylserine ethyl ester:

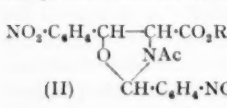
$$2NO_2\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot CO_2Et \xrightarrow{H_2O} \underset{\substack{CH(OH)\cdot C_6H_4\cdot NO_2\\ erythro}}{NO_2\cdot C_6H_4\cdot CH{:}N\cdot CH\cdot CO_2Et} + NH_2\cdot CH_2\cdot CO_2Et$$

Conversely, the interaction of the latter product with an excess of glycine ethyl ester leads to *threo-p*-nitrophenylserine ethyl ester:

$$\underset{\substack{CH(OH)\cdot C_6H_4\cdot NO_2\\ erythro}}{NO_2\cdot C_6H_4\cdot CH{:}N\cdot CH\cdot CO_2Et} + NH_2\cdot CH_2\cdot CO_2Et \longrightarrow \underset{threo}{NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH(NH_2)\cdot CO_2Et} + NO_2\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot CO_2Et$$

Accordingly, condensation of *p*-nitrobenzaldehyde with an excess of glycine ethyl ester without solvent leads directly to the crystalline *threo-p*-nitrophenylserine ethyl ester (Elphimoff-Felkin, Felkin, and Welvart, *Compt. rend.*, 1952, **234**, 1627; cf. *ibid.*, p. 1564).

(*e*) The *threo*- and the *erythro*-form of *N*-(*p*-nitrobenzylidene)-*p*-nitrophenylserine ethyl ester, upon acetylation, give different acetyl derivatives. Their structure is that of *N*-acetyl derivatives of the corresponding oxazolidines (ethyl 3-acetyl-2 : 5-di-*p*-nitrophenyloxazolidine-4-carboxylate) (II). Both show in the infra-red spectrum a band (1660 cm.$^{-1}$) characteristic of a disubstituted amide (see Richards and Thompson, *J.*, 1947, 1248; E. Bergmann, Zimkin, and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 188) (regarding this rearrangement, see E. Bergmann, Gil-Av, and Pinchas, *J. Amer. Chem. Soc.*, 1953, **75**, 358). Also the ultra-violet spectra of the two acetyl derivatives show only a maximum at 2655 Å (log ε: *threo*, 4·35; *erythro*, 4·32) and a minimum at 2375 Å (log ε: *threo*, 3·83; *erythro*, 3·80); the corresponding Schiff bases absorb at 2700 (*threo*; log ε 4·39) and 2710 Å (*erythro*; log ε 4·42) (minima: *threo*, 2280 Å, log ε 3·91; *erythro*, 2330 Å, log ε 3·87) respectively, owing to the more extended conjugated system. Analogously, 2-hydroxy-*N*-*p*-nitrobenzylidene-ethylamine absorbs at 2750 Å, and 2 : 4 : 5 : 5-tetramethyl-2-*m*-nitrophenyloxazolidine at 2650 Å (E. Bergmann, Hirshberg, Pinchas, and Zimkin, *Rec. Trav. chim.*, 1952, **71**, 192).

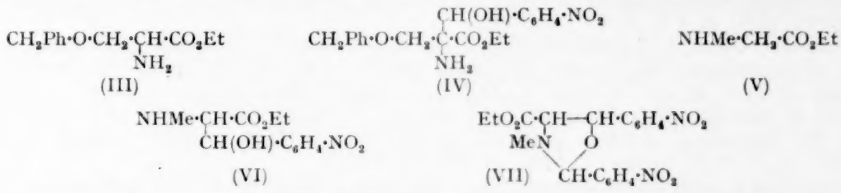


(II)

McCasland and Horswill (*J. Amer. Chem. Soc.*, 1951, **73**, 3923) have reported a number of cases in which Schiff bases derived from β-hydroxy-amines are converted into the *N*-acyl derivatives of the isomeric oxazolidines, and similar observations have been made in the thiazolidine and the tetrahydroglyoxaline series. Apart from the present case, however, diastereomeric pairs of oxazolidines are known only in the *N*-acylbenzylidene derivatives of the two 2-amino*cyclo*hexanols (McCasland and Horswill, *loc. cit.*) and in the benzylidene derivatives of ephedrine and *ψ*-ephedrine (Schmidt, *Arch. Pharm.*, **1914**, **252**, 89; Davies, *J.*, 1932, 1580). In the thiazolidine series, an analogous pair has been prepared from thio-DL-threonine and thio-DL-*allo*threonine, with ethyl benzylpenaldate (Clarke, Johnson, and Sir R. Robinson, "The Chemistry of Penicillin," Oxford Univ. Press, 1949, pp. 498, 525, 642).

(*f*) The Schiff *threo*-base used in these experiments has been prepared from the *threo*-ester by azeotropic condensation in boiling benzene (see Holland and Nayler, *loc. cit.*); like the *erythro*-isomer, it is a well-crystallised, stable compound; its infra-red spectrum proves the Schiff base structure (C:N and OH absorption).

*Photochemical Condensations.*—The activity of the methylene group in α-amino-esters can be enhanced by irradiation to the point where the presence of the azomethine bond becomes superfluous for the aldol-condensation with aromatic aldehydes. *O*-Benzylserine ethyl ester (III) and *p*-nitrobenzaldehyde thus gave ethyl α-amino-α-benzyloxymethyl-β-hydroxy-β-*p*-nitrophenylpropionate (IV), the structure of which follows from



the presence of a free amino-group (van Slyke) and the infra-red absorption spectrum [absence of an azomethine system; presence of a hydroxyl group, hydrogen-bonded to the nitrogen atom (3275 cm.$^{-1}$; cf. E. Bergmann, Zimkin, and Pinchas, *J. Amer. Chem. Soc.*, 1953, **75**, 68)]. It may well be that the relative inactivity of the amino-group in (III), shown in the inability to condense with the aromatic aldehyde, is due to its hydrogen bonding with the ether-oxygen atom.

An analogous photochemical reaction appears to take place—at least primarily—if sarcosine ethyl ester (V) and *p*-nitrobenzaldehyde in methanol are exposed to sunlight. However, instead of the expected product (VI) a compound was obtained which was built up from one mol. of (V) and two of *p*-nitrobenzaldehyde. On the basis of the analytical data and the infra-red spectrum, formula (VII) of an ethyl 3-methyl-2 : 5-di-*p*-nitrophenyloxazolidine-4-carboxylate is assumed. It is derived from (VI) by a reaction normal for secondary β-hydroxy-amines (see E. Bergmann, Zimkin, and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 229, 237).

When the mixtures of the esters of phenylalanine, glutamic, or aspartic acid with *p*-nitrobenzaldehyde were exposed to sunlight, no condensation reaction took place (cf. E. Bergmann and Bendas, *Bull. Israeli Res. Council*, 1952, **2**, 198). *NN*-Dimethylglycine ethyl ester gave a positive response; however, the reaction was accompanied by elimination of a methyl group, and the product proved identical with that formed from sarcosine ethyl ester.

*Infra-red Spectra.*—For a number of the substances involved in this investigation, the infra-red spectra were studied. It was hoped that the diastereomeric pairs would show differences, as it seemed possible that the strength of the hydrogen bonds which exist in these β-hydroxy-amine systems (see E. Bergmann, Zimkin, and Pinchas, *loc. cit.*) depends on the configuration. This, however, was not the case; the spectra of *threo*- and *erythro*-*p*-nitrophenylserine ethyl esters are practically identical. Also the spectra of the hydrochlorides of the two esters which were studied in form of a mull in paraffin oil, are fairly

similar although there exist certain differences. The two diastereomeric *ON*-diacetyl derivatives give identical spectra from 3400 to 1000 cm.$^{-1}$, except that the band at 1610 cm.$^{-1}$ was stronger for the *erythro*-compound; beyond 1000 cm.$^{-1}$, the *threo*-compound shows bands at 965, 920, 855, and 840 cm.$^{-1}$, whilst the *erythro*-isomer absorbs at 950, 935, 915, 900, and 855 cm.$^{-1}$.

## Experimental

*1-Carbethoxymethylpyridinium Bromide.*—A mixture of pyridine (40 g.) and ethyl bromoacetate (84 g.) was stirred at 0° and subsequently at 50°, and the cake formed recrystallised from a mixture of ethyl methyl ketone and *iso*propyl alcohol. The salt (53 g., 43%) is slightly hygroscopic.

*1-(1-Carboxy-2-p-chlorophenyl-2-hydroxyethyl)pyridinium Betaine.*—When a solution of sodium hydroxide (0·4 g.) in methanol was added to a mixture of the foregoing salt (2·5 g.) and *p*-chlorobenzaldehyde (1·4 g.), an exothermic reaction took place. At 0°, the *product* crystallised; it was washed with ice-cold water and recrystallised from 90% methanol as prismatic needles, m. p. 146—147° (decomp.) (Found: C, 60·5; H, 4·4; N, 4·9; Cl, 12·7. $C_{14}H_{12}O_3NCl$ requires C, 60·6; H, 4·3; N, 5·1; Cl, 12·8%).

Similarly, *o*-chlorobenzaldehyde gave, after recrystallisation from methanol, the *o-chloro*-isomer as octahedra, m. p. 161° (decomp.) (Found: C, 60·7; H, 4·5; N, 4·8; Cl, 12·5. $C_{14}H_{12}O_3NCl$ requires C, 60·6; H, 4·3; N, 5·1; Cl, 12·8%). A small quantity of material did not dissolve in methanol; by recrystallisation from glacial acetic acid, it was obtained as prisms, m. p. 152° (decomp.). The analysis pointed to the structure *1-(1-carboxy-2-o-chlorophenyl-2-hydroxyethyl)pyridinium acetate* (Found: C, 56·9; H, 5·0; N, 5·0; Cl, 10·7. $C_{16}H_{16}O_5NCl$ requires C, 57·0; H, 4·7; N, 4·7; Cl, 10·4%).

*1-(Carboxy-2-hydroxy-2-p-nitrophenylethyl)pyridinium Betaine.*—Condensation as above, with 1·5 g. of *p*-nitrobenzaldehyde, gave the *betaine*, prisms, m. p. 159° (decomp.) (from methanol) (Found: C, 58·4; H, 4·3; N, 10·0. $C_{14}H_{12}O_5N_2$ requires C, 58·3; H, 4·2; N, 9·7%). A small amount of material, which was insoluble in methanol, crystallised from acetic acid in platelets, m. p. 161° (decomp.). Analyses pointed to a *product* $C_{17}H_{18}O_8N_2$ (Found: C, 53·9; H, 4·6; N, 7·8. $C_{17}H_{18}O_8N_2$ requires C, 54·0; H, 4·8; N, 7·4%).

*N-(5-Nitro-2-furfurylidene)*-erythro(?)-β-*(5-nitro-2-furyl)serine Ethyl Ester and* erythro(?)-β-*(5-Nitro-2-furyl)serine Ethyl Ester Hydrochloride.*—5-Nitrofurfuraldehyde was prepared by nitration of furfuraldehyde diacetate and subsequent hydrolysis (Gilman and Wright, *J. Amer. Chem. Soc.*, 1930, **52**, 2550, 4165). To a solution of the aldehyde (2·82 g.) in dry ether (20 c.c.), freshly distilled glycine ethyl ester (0·90 g.) was added. [The excess of the aldehyde (25%) is necessary, as otherwise the solution darkens.] After 12 hr., crystals of the *Schiff base* (0·30 g.) had separated. Washed with ether and recrystallised from propyl alcohol or benzene, they had m. p. 136° (Found: C, 46·0; H, 3·7; N, 11·5; $OC_2H_5$, 12·5; active H, 0·29. $C_{14}H_{13}O_9N_3$ requires C, 45·8; H, 3·5; N, 11·4; $OC_2H_5$, 12·3; 1 H, 0·27%).

When alcoholic hydrochloric acid was added to the mother-liquor, a brown oil separated which was washed with ether and triturated with chloroform, whereupon it solidified (yield, 1·1 g.). Recrystallised from chloroform or *iso*propyl alcohol, the ester *hydrochloride* had m. p. 156° (Found: C, 38·3; H, 4·3; N, 10·0; OEt, 15·9; active H, 0·8. $C_9H_{13}O_6N_2Cl$ requires C, 38·6; H, 4·6; N, 10·0; OEt, 16·1; 2 H, 0·8%).

The same products were obtained when the condensation was carried out in ethyl alcohol at room temperature (24 hr.).

erythro(?)-4-*Methyl-3-nitrophenylserine Methyl Ester Hydrochloride.*—A solution of 4-methyl-3-nitrobenzaldehyde (6·3 g.) and glycine methyl ester (1·8 g.) in methanol (20 c.c.) was kept at room temperature for 24 hr.; then methanolic hydrogen chloride (15 c.c., containing 1·5 g. of HCl) and an excess of ether were added. The semi-solid bottom layer was triturated with *iso*propyl alcohol (yield, 0·5 g.) and recrystallised from the same solvent. The ester *hydrochloride* formed leaflets, m. p. 181° (decomp.) (Found: C, 45·0; H, 5·0; N, 9·3; Cl, 12·0. $C_{11}H_{15}O_5N_2Cl$ requires C, 45·5; H, 5·2; N, 9·6; Cl, 12·1%).

4-Methyl-3-nitrobenzaldehyde (Hanzlik and Bianchi, *Ber.*, 1899, **32**, 1288; Gattermann, *Annalen*, 1906, **347**, 347), purified by distillation *in vacuo*, had b. p. 162°/25 mm. [from 12 g. of *p*-tolualdehyde, 12·5 g. (76%) were obtained].

erythro(?)-m-*Nitrophenylserine Ethyl Ester Hydrochloride.**—This had been obtained by Bergmann *et al.* (*loc. cit.*) by condensation of *m*-nitrobenzaldehyde and glycine ethyl ester in

* The m. p. of *m*-nitrophenylserine ethyl ester hydrochloride is 191° (decomp.), not 131° (decomp.), as erroneously reported by Bergmann *et al.* (*loc. cit.*).

ethanol; no analyses had been given. The *salt* formed leaflets, m. p. 184° (decomp.), from amyl alcohol (Found: C, 45·7; H, 5·3; N, 9·4; Cl, 12·1. $C_{11}H_{15}O_3N_2Cl$ requires C, 45·5; H, 5·2; N, 9·6; Cl, 12·1%).

erythro-N-(p-*Nitrobenzylidene*)-p-*nitrophenylserine Methyl Ester*.—When *p*-nitrobenzaldehyde (7·5 g.) and glycine methyl ester (2·3 g.) were kept in a little methanol at room temperature for 24 hr., the condensation *product* (9·0 g.) separated. After recrystallisation from *iso*propyl alcohol, it had m. p. 160° (Found: C, 54·9; H, 3·9; N, 11·0; OMe, 8·4; active H, 0·3. $C_{17}H_{15}O_7N_3$ requires C, 54·7; H, 4·0; N, 11·2; OMe, 8·3; 1 H, 0·3%).

erythro(?)-2 : 6-*Dichlorophenylserine Ethyl Ester Hydrochloride*.—In Part I, the parallel reaction with the methyl ester was described. The mixture of 2 : 6-dichlorobenzaldehyde (2·5 g.), glycine ethyl ester (0·7 g.), and anhydrous alcohol (10 c.c.) was refluxed for 2 hr., and ether (100 c.c.) and alcoholic 4N-hydrochloric acid (1·5 c.c.) were added. After filtration from a small precipitate and concentration of the solution, the *ester hydrochloride* crystallised. Recrystallised from alcohol–ether, it had m. p. 170° (decomp.) (Found: C, 42·0; H, 4·6; N, 4·7; Cl, 33·4. $C_{11}H_{14}O_3NCl_3$ requires C, 42·5; H, 4·5; N, 4·5; Cl, 33·2%).

threo-O-*Acetyl*-N-*dichloroacetyl*-p-*nitrophenylserine Ethyl Ester*.—This was prepared according to Huebner and Scholz (*loc. cit.*) by nitration of *O*-acetyl-*N*-dichloroacetyl-*threo*-*p*-phenylserine ethyl ester (4 g.) with fuming ntric acid (4 c.c.) and concentrated sulphuric acid (4 c.c.) (30 min.). Upon dilution with ice, an oil separated which solidified quickly. Recrystallised from 50% methanol, the ester formed shiny needles, m. p. 127—128°.

threo-N-(p-*Nitrobenzylidene*)-p-*nitrophenylserine Ethyl Ester*.—*threo*-*p*-Nitrophenylserine ethyl ester (Elphimoff-Felin, Felkin, and Welvart, *loc. cit.*) (3·7 g.) and *p*-nitrobenzaldehyde (2·2 g.) were subjected to azeotropic condensation in presence of boiling benzene (35 c.c.). After 3 hr., the solvent was evaporated and the residue triturated at 0° with methanol and a little nitromethane and recrystallised twice from *iso*propyl alcohol. It had m. p. 120°.

*Ethyl* 3-*Acetyl*-2 : 5-*di*-p-*nitrophenyloxazolidine*-4-*carboxylates*.—(a) threo-*Form*. The preceding substance (0·5 g.) was refluxed for 1 hr. with acetic anhydride (5 c.c.). The mixture was diluted with water, and the resulting solid triturated with methanol and recrystallised from *iso*propyl alcohol. The *ester* had m. p. 172° (Found: C, 56·2; H, 4·5; N, 9·9. $C_{20}H_{19}O_8N_3$ requires C, 56·0; H, 4·4; N, 9·8%).

(b) erythro-*Form*. The same reaction was carried out with *N*-(*p*-nitrobenzylidene)-*erythro*-*p*-nitrophenylserine ethyl ester (Part I). The *product* had m. p. 172°, but depressed the m. p. of the compound obtained as under (a) to 152° (Found: C, 56·0; H, 4·7; N, 9·9; OEt, 10·0. $C_{20}H_{19}O_8N_3$ requires C, 56·0; H, 4·4; N, 9·8; OEt, 10·5%).

The infra-red spectrum was measured in chloroform (16 mg. and 1 c.c. of solvent). The hydroxyl and the C:N bands were absent, the band of a disubstituted acetamide appeared at 1600 cm.$^{-1}$, and that of the carbethoxy-group at 1730 cm.$^{-1}$. Two bands, at 1620 and 1525 cm.$^{-1}$, respectively, are very likely due to the phenyl groups.

*Azeotropic Condensations*.—(*a*) *p*-Nitrobenzaldehyde (0·5 g.) and glycine ethyl ester (5·2 g.) in benzene (50 c.c.) were subjected to azeotropic distillation. After 3 hr., the solvent was distilled off and the resinous residue treated with methanolic hydrochloric acid (30 c.c.; containing 3 g. of HCl) and an excess of ether. An oil separated which solidified on standing (yield, 4·5 g., 31%). Recrystallised from amyl alcohol, the *erythro*-*p*-nitrophenylserine ethyl ester hydrochloride formed prisms, m. p. 188° (decomp.) (Bergmann *et al.*, *loc. cit.*, give m. p. 189°). The same result was obtained when half of the above quantity of ethyl ester was employed, the yield being 3·9 g. (54%).

(*b*) *m*-Nitrobenzaldehyde (7·5 g.) and glycine ethyl ester (2·6 g.) were condensed as above. With methanolic hydrochloric acid (15 c.c., containing 1·5 g. of HCl), the hydrochloride (6 g., 83%) was obtained. From 2-nitropropane it formed leaflets; when crystallisation set in, a few drops of acetone were added which prevented the product from forming an oil. *erythro*(?)-*m*-Nitrophenylserine ethyl ester hydrochloride had m. p. 182° (decomp.) (Bergmann *et al.*, *loc. cit.*, give m. p. 180—184°).

(*c*) The mixture of glycine methyl ester (2·4 g.) and *m*-nitrobenzaldehyde (8·2 g.) with benzene (50 c.c.) was subjected to azeotropic distillation, which liberated quickly 1 c.c. of water. The solution was filtered from a little insoluble material and evaporated to dryness. The residual oil, on treatment with methanolic hydrochloric acid and an excess of ether, gave a thick precipitate of erythro(?)-m-*nitrophenylserine methyl ester hydrochloride*, which crystallised from butanol in leaflets (1·1 g.), m. p. 190° (decomp.) (Found: C, 43·8; H, 4·8; N, 10·0, 9·9. $C_{10}H_{13}O_5N_2Cl$ requires C, 43·5; H, 4·7; N, 10·1%).

(*d*) 4-Methyl-3-nitrobenzaldehyde (6·3 g.) and glycine methyl ester (1·8 g.) were condensed

as above. The hydrochloride of *erythro*(?)-4-methyl-3-nitrophenylserine methyl ester which separated on addition of methanolic hydrochloric acid (15 c.c., containing 1·5 g. of HCl) and an excess of ether, formed an oil which was triturated with acetone. The crystals (0·5 g., 8%) were recrystallised from *iso*propyl alcohol, forming prisms, m. p. 179° (decomp.). The substance was identical with the ester described on p.

(*e*) 2 : 6-Dichlorobenzaldehyde (2·5 g.), freshly distilled glycine ethyl ester (0·7 g.), and benzene (20 c.c.) were subjected to azeotropic distillation for 30 min. After cooling, anhydrous ether (100 c.c.) and alcoholic 4N-hydrochloric acid (1·5 c.c.) were added. Thus, *erythro*(?)-2 : 6-dichlorophenylserine ethyl ester hydrochloride (2 g.) was obtained; recrystallised from a little alcohol it melted at 170°. It did not depress the m. p. of the ester described before.

(*f*) 5-Nitrofurfuraldehyde (2·80 g.), glycine ethyl ester (1·0 g.), and benzene (20 c.c.) were refluxed azeotropically for 30 min. Upon cooling, *N*-(5-nitro-2-furfurylidene)-*erythro*(?)-β-(5-nitro-2-furyl)serine ethyl ester (1·0 g.) crystallised; after recrystallisation from alcohol, it melted at 134° and was identical with the Schiff base obtained as described before.

Addition of alcoholic 3N-hydrochloric acid (2·5 c.c.) to the benzene mother-liquor precipitated *erythro*(?)-β-(5-nitro-2-furyl)serine ethyl ester hydrochloride, m. p. 160° (from alcohol), identical with the hydrochloride described before.

(*g*) A different course of the azeotropic condensation was observed in the reaction between glycine methyl ester and *p*-chlorobenzaldehyde. The reaction between the ester (2·2 g.) and *p*-chlorobenzaldehyde (3·5 g.) in benzene (50 c.c.) set in at once (turbidity); the theoretical quantity of water collected in the receiver after azeotropical distillation for 30 min. The product was recrystallised from *iso*propyl alcohol and melted at 163°. The analysis pointed to the formula of N : α-*di*-p-*chlorobenzylideneglycine methyl ester*, which would imply that the *N*-(*p*-chlorobenzylidene)-*p*-chlorophenylserine ester had been formed, but had split off water, presumably during distillation (Found: C, 60·9; H, 4·1; N, 4·5; Cl, 20·9; OMe, 9·8%; *M*, 304. $C_{17}H_{13}O_2NCl_2$ requires C, 61·1; H, 3·9; N, 4·2; Cl, 21·3; OMe, 9·3%; *M*, 334).

The infra-red spectrum (0·023 g. in 1 c.c. of chloroform; cell-thickness, 0·1 mm.) showed the following bands (the most intense in *italics*): ***1692***, 1609, 1577, 1476, 1430, 1297, 1103, ***1084***, 1008, 978 cm.$^{-1}$. It is assumed that the strong band at 1692 cm.$^{-1}$ is due to the superposition of the ester absorption and that of the C:N double bond (Colthup, *J. Opt. Soc. America*, **1950**, **40**, 397). which also absorbs at 1577 cm.$^{-1}$ (at the same wave-number as phenyl). The band at 1084 cm.$^{-1}$ is undoubtedly that of the *p*-chlorophenyl radical; it appears also in chlorobenzene, *p*-chlorotoluene, and *p*-chlorophenol (Barnes *et al.*, "Infra-red Spectroscopy," New York, 1944).

The ultra-violet spectrum (in $CHCl_3$) showed a pronounced maximum at 2715 Å and a less distinct one at 3000 Å. This substance is, therefore, less absorbent than the similar 1 : 4-diphenylbutadiene (Jones, *Chem. Reviews*, **1943**, **32**, 1); this difference may be accounted for by steric inhibition of the conjugation through the esterified carboxyl group as the azlactones absorb at 3300—3600 Å (Bennett and Hoerger, *J. Amer. Chem. Soc.*, 1952, **74**, 5975; cf. Bassi, Deulofeu, and Ortega, *ibid.*, 1953, **75**, 171).

*Reactions with Glycine Benzyl Ester.*—(*a*) A solution of ammonia (2 g.) in chloroform (66 c.c.) was agitated for 24 hr. with glycine benzyl ester hydrobromide (13 g.) (D. Ben-Ishai and Berger, *J. Org. Chem.*, 1952, **17**, 1564). After addition of anhydrous ether (50 c.c.), the solution was filtered and evaporated *in vacuo* to dryness. The crude ester (8·2 g., 94%) was used for experiment.

(*b*) threo-p-*Nitrophenylserine benzyl ester*. When *p*-nitrobenzaldehyde (3·0 g.) and glycine benzyl ester (5 g., 1·5 mols. per mol. of aldehyde) were mixed at room temperature, an exothermic reaction set in, and the mass became a brown semi-solid. This was triturated with ether and a little acetone, and the crystalline ester filtered off (2·8 g., 44%). From *iso*propyl alcohol, the *ester* crystallised in prisms, m. p. 130° (Found: C, 60·5; H, 5·0; N, 8·8. $C_{16}H_{16}O_5N_2$ requires C, 60·7; H, 5·1; N, 8·9%).

(*c*) erythro(?)-p-*Chlorophenylserine benzyl ester hydrochloride*. To a solution of sodium methoxide (0·54 g.) in methanol (25 c.c.), there were added glycine benzyl ester hydrobromide (2·5 g.) and *p*-chlorobenzaldehyde (2·8 g.). After 48 hr. at room temperature, an oil had separated. Upon addition of 12% methanolic hydrochloric acid (6 c.c.) and an excess of ether, the oil dissolved, and a fine precipitate appeared which was recrystallised from *iso*propyl alcohol. The *ester hydrochloride* formed needles, m. p. 232° (decomp.) (Found: C, 56·0; H, 5·0; N, 4·1; Cl, 20·5; active H, 0·82. $C_{16}H_{17}O_3NCl_2$ requires C, 56·1; H, 5·0; N, 4·1; Cl, 20·7; 3 H, 0·88%).

*Ethyl* 3-*Methyl*-2 : 5-*di*-p-*nitrophenyloxazolidine*-4-*carboxylate* (VII).—A methanolic solution

of sarcosine ethyl ester (1·3 c.c.) (E. Fischer, *Ber.*, 1901, **34**, 452; b. p. 60°/10 mm.) and *p*-nitrobenzaldehyde (1·5 g.) was exposed to direct sunlight in a quartz vessel. Evaporation gave an oil which crystallised on trituration with methanol containing a small quantity of acetone. After recrystallisation from *iso*propanol, the *ester* had m. p. 171° (Found: C, 56·5; H, 4·7; N, 10·8; OEt, 10·9; NMe, 6·9. $C_{19}H_{19}O_7N_3$ requires C, 56·8; H, 4·7; N, 10·4; OEt, 11·2; NMe, 7·2%).

The infra-red spectrum was investigated in chloroform solution (0·025 g. in 1 c.c. of solvent; cell thickness: 0·1 mm.). Absorption in the hydroxyl region was completely lacking; at 1747 cm.$^{-1}$ the carboxyl band, and at 1606 cm.$^{-1}$ the phenyl absorption, were observed. In the oxazolidine region (E. Bergmann, Zimkin, and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 168 ff.), bands appeared at 1179, 1116, 1068, and 1045 cm.$^{-1}$. The band at 1116 cm.$^{-1}$ may also be accounted for as that of the *p*-substituted benzene nucleus.

O-*Benzylserine*.—For the preparation of αβ-dibromopropionic acid, the oxidation of 2 : 3-dibromopropanol (Beilstein's "Handbuch," Vol. II, p. 258) was employed. Oxidation (of 100 g., b. p. 110—112°/15 mm.) with a mixture of concentrated (140 g.) and fuming (30 g.) nitric acid at 0° for 12 hr. and at room temperature for a further 24 hr. gave an 80% yield of αβ-dibromopropionic acid, b. p. 150—160°/23 mm., m. p. 61° (ethyl ester, b. p. 86—87°/7 mm.).

By the method of Wood and du Vigneaud (*J. Biol. Chem.*, 1940, **134**, 413), ethyl αβ-dibromopropionate (260 g.) was converted, by means of a solution of sodium (24 g.) in benzyl alcohol (500 c.c.), into ethyl β-benzyloxy-α-bromopropionate. This was isolated in crude form by evaporation of the excess of benzyl alcohol at 60°/0·1 mm., and transformed by treatment with ammonia at 100° into *β-benzyloxyalanine*. The aqueous solution obtained was repeatedly evaporated to dryness *in vacuo* and the solid product washed with cold water until the filtrate gave a negative bromide test. Recrystallisation from water gave platelets, m. p. 218° (50 g., 26%) (Found: C, 61·7; H, 6·7; N, 7·3. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7; N, 7·2%).

O-*Benzylserine Ethyl Ester Hydrochloride* (III).—A suspension of the amino-acid (20 g.) in anhydrous ethanol (100 c.c.) was saturated with gaseous hydrogen chloride and the mixture heated until a clear solution was obtained (5 min.). The product was evaporated to dryness *in vacuo* and the residue dissolved in a little alcohol and precipitated with dry ether. Thus, a yield of 18 g. (68%) of the *salt* (III) was obtained which had m. p. 102° (Found: C, 55·4; H, 6·8; N, 5·6. $C_{12}H_{18}O_3NCl$ requires C, 55·5; H, 7·0; N, 5·4%).

*Ethyl α-Amino-α-benzyloxy-β-hydroxy-β-p-nitrophenylpropionate* (IV).—At 0° the foregoing ester hydrochloride (4 g.) was stirred with chloroform (10 c.c.) which contained 2% of gaseous ammonia (Hillman, *Chem. Abs.*, 1949, **43**, 7425). The filtered solution was evaporated to dryness *in vacuo* (at 20°) and the residue dissolved in anhydrous alcohol. *p*-Nitrobenzaldehyde (3 g.) was added and the solution kept in the sun for 2 days, the desired *product* (2 g.) separating. Washing with ether and recrystallisation from *iso*propyl alcohol gave prisms, m. p. 136° [Found: C, 61·2; H, 5·7; N, 7·5; OEt, 12·0; amino-N, 3·7%; *M*, 350 (in boiling benzene). $C_{19}H_{22}O_6N_2$ requires C, 61·0; H, 5·9; N, 7·5; $OC_2H_5$, 12·0; amino-N, 3·7%; *M*, 374]. The infra-red spectrum (0·065 g. and 1 c.c. of chloroform; cell-thickness 0·1 mm.) of (IV) shows no band in the absorption region of the C:N double bond. The following bands have been measured and identified: 3275 (OH, hydrogen-bonded), 1731 ($CO_2R$), 1609 (aromatic double bond), 1349 ($NO_2$ in conjugation), 1183 (*para*-substituted phenyl), 1133 (ether grouping), and 1107 cm.$^{-1}$ (*para*-substituted phenyl) (cf. Randle and Whiffen, *J.*, 1952, 4153).

For the infra-red spectra we are indebted to Dr. D. Ginsburg, while he was working at Harvard University, and to Dr. S. Pinchas, Optics Department, Weizmann Institute of Science, Rehovoth. This investigation was carried out under the auspices of the Scientific Department, Israeli Ministry of Defence, and is published with its permission.

Laboratories, Scientific Department, Israeli Ministry of Defence,
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## 523. 1 : 1′-*Difluorodianthron-9-ylidene and an Attempted Synthesis of* 4 : 4′-*Dibromodianthron-9-ylidene.*

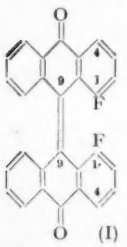
By Ernst D. Bergmann and H. J. E. Loewenthal.

Although 1 : 1′-substituents such as OMe, Br, or Me destroy the thermochromism of dianthron-9-ylidene, the small fluorine atom does not, since 1 : 1′-difluorodianthron-9-ylidene (I), which has been synthesized, is thermochromic.

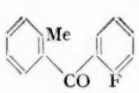
The bromine atom in 1-bromoanthraquinone is unusually labile.

It had been shown that substituents (*e.g.*, Br, Me, OMe) in the 1 : 1′-positions of dianthron-9-ylidene destroy the thermochromism of the parent substance (Bergmann and Loewenthal, *Bull. Soc. chim.*, 1952, **19**, 66). In view of the theoretical significance of this effect, it seemed worthwhile to establish whether it is dependent on the volume of the substituents. This is indeed so. 1 : 1′-Difluorodianthron-9-ylidene (I) has been synthesized and proved thermochromic; its solutions in diphenyl ether became, reversibly, green on heating.

For the synthesis of (I), 4-fluoroanthrone (V) was prepared. *o*-Fluorobenzonitrile and *o*-tolylmagnesium bromide gave 2′-fluoro-2-methylbenzophenone (II). Selenium dioxide, which has been applied to similar cases before (*Organic Reactions*, 1949, **5**, 173), oxidized (II) to 2-*o*-fluorobenzoylbenzoic acid (III). The corresponding 2-*o*-fluorobenzylbenzoic acid (IV) was cyclized to (V). This was dehydrogenated with ferric chloride (Dimroth, *Ber.*, 1901, **34**, 219) to the corresponding dianthron-9-yl (VI), and the enol form of the latter with *p*-benzoquinone (Schönberg and Ismail, *J.*, 1944, 307) gave the desired



(I)



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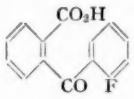

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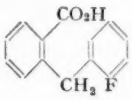

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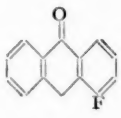
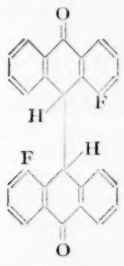


(V)

1 : 1′-difluorodianthron-9-ylidene (I). It is interesting that in distinction from other 1 : 1′-disubstituted dianthronyls, (VI) enolizes as easily as the unsubstituted parent compound.

In connection with these experiments, an attempt was made to prepare 4 : 4′-dibromodianthron-9-ylidene, the only symmetrically dibrominated compound of this series still unknown. This was thwarted by the surprising lability of the bromine atoms, which is paralleled by, but far greater than, that of the bromine atoms in bromo-substituted *o*-benzoylbenzoic acids towards alkaline reducing agents (Bergmann and Loewenthal, *loc. cit.*). As the routes analogous to the synthesis of (V) appeared to be very cumbersome, the possibility of the reduction of 1-bromoanthraquinone to 1-bromoanthrone (VII) was explored; it was known (Attree and Perkin, *J.*, 1931, 144; Barnett and Matthews, *J.*, 1923, **123**, 2549) that, *e.g.*, 1-chloro- and 1-methoxy-anthraquinone give, by this method, the corresponding 1-substituted anthrones. Indeed, reduction of 1-bromoanthraquinone with copper and concentrated sulphuric acid gave a product which was extremely unstable in air and for this reason could not be the known stable alternative reduction product 4-bromoanthrone. Ferric chloride oxidation of the crude product, which is considered to be (VII), gave a dianthron-9-yl, presumably the 4 : 4′-dibromo-compound (VIII); but in spite of repeated recrystallisations, bromine analysis gave low values. Further dehydrogenation of (VII) with *p*-benzoquinone gave a strongly thermochromic product which, however, according to the bromine analysis contained only 24% of a dibromodianthron-9-ylidene.

The instability of the bromine atom in these compounds is somewhat surprising; perhaps it is due to the existence of zwitterionic forms, *e.g.*, (VII*a*). The halogen atoms in 1-halogenoanthraquinones are known to be readily reduced out (cf. Kirchner, *Annalen*,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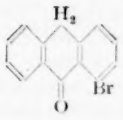
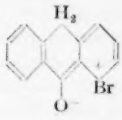
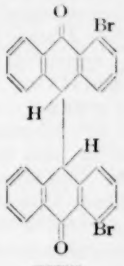

(VII)


(VII*a*)


(VIII)

1887, **238**, 345); *e.g.*, refluxing these compounds in nitrobenzene in presence of copper powder and potassium acetate causes hydrogenolysis of the C–Hal bond (Ullmann and Minajeff, *Ber.*, 1912, **45**, 687).

## Experimental

2′-*Fluoro*-2-*methylbenzophenone* (II).—From *o*-fluorobenzoic acid (Schiemann, *J. pr. Chem.*, 1934, **140**, 97), the nitrile (b. p. 92—95°/22 mm.) was prepared *via* the amide, according to Borsche and Wagner-Roemmich (*Annalen*, 1941, **546**, 273), in 62% yield. A solution of the nitrile (17·5 g.) in dry benzene (100 ml.) was added to *o*-tolylmagnesium bromide [from *o*-bromotoluene (30·4 g.) and magnesium (4·1 g.) in ether (125 ml.)]. The ether was distilled off, and the benzene solution refluxed for 7 hr. and worked up as usual for this type of reaction (see, *e.g.*, Schlenk and Bergmann, *ibid.*, 1928, **464**, 34). The *ketone* (II) distilled as an almost colourless oil, b. p. 125—130/1 mm. (23·5 g., 76·5%), $n_D^{20}$ 1·5800 (Found : C, 78·8; H, 5·1. $C_{14}H_{11}OF$ requires C, 78·5; H, 5·1%). The 2 : 4-dinitrophenylhydrazone separated after several days. Recrystallization from ethyl acetate–ethanol gave orange needles, m. p. 184°.

2-*o*-*Fluorobenzoylbenzoic Acid* (III).—The preceding ketone (8·7 g.) and selenium dioxide (11 g.) were refluxed together in nitrobenzene (50 ml.) for 4 hr. After cooling, the mixture was diluted with ether, filtered from selenium, and extracted with a total of 90 ml. of 10% sodium carbonate solution. The alkaline extracts were saturated with carbon dioxide, treated with charcoal, and filtered. Acidification gave the crude *acid*, m. p. 138—139·5° (5·2 g., 56%). Recrystallization from benzene–heptane and subsequently from water raised the m. p. of the colourless needles to 140° (Found : C, 69·1; H, 4·1. $C_{14}H_9O_3F$ requires C, 68·9; H, 3·7%).

2-*o*-*Fluorobenzylbenzoic Acid* (IV).—This acid was obtained from the keto-acid (3·8 g.) by means of activated zinc dust and ammonia (Bergmann and Loewenthal, *loc. cit.*) (yield, 3·4 g., 94·5%). The *acid* formed colourless needles, m. p. 116—117°, from heptane and depressed the m. p. of *o*-benzylbenzoic acid which melts at the same temperature (Found : C, 72·5; H, 4·9. $C_{14}H_{11}O_2F$ requires C, 73·0; H, 4·8%).

4-*Fluoroanthrone* (V).—Cyclisation of the preceding acid (3·2 g.) with sulphuric acid (20 ml.) at room temperature proceeded slowly. Recrystallization of the *anthrone* from methanol gave 2·25 g. (76%) of yellowish needles, m. p. 143° (Found : C, 79·1; H, 4·5. $C_{14}H_9OF$ requires C, 79·2; H, 4·3%).

1 : 1′-*Difluorodianthron*-9-*yl* (VI).—A mixture of 4-fluoroanthrone (V) (2·2 g.), glacial acetic acid (11 ml.), ferric chloride (2·2 g.), and sodium acetate (2·2 g.) was kept at 100° for 1·5 hr. After cooling and dilution with ice-cold methanol, the greyish crystals were filtered off (yield, 1·8 g.). Addition of water to the filtrate gave a second crop of 0·2 g. (total yield, 91%). Recrystallization from benzene–heptane gave the *product* as slightly yellow prisms, m. p. 212·5—213° (Found : C, 79·2; H, 4·0. $C_{28}H_{16}O_2F_2$ requires C, 79·6; H, 3·7%).

1 : 1′-*Difluorodianthron*-9-*ylidene* (I).—The dianthronyl (1·4 g.) was enolized (Bergmann and Loewenthal, *loc. cit.*) in less than 10 min. Oxidation of the dianthranol with *p*-benzoquinone proceeded without occurrence of the usual transient green colour; 1 : 1′-*dianthronylidene* was precipitated immediately in 86% yield (1·2 g.). From chloroform–xylene, it crystallized in very pale yellow needles, m. p. >360°. It was slightly, but definitely thermochromic (reversibly) in boiling diphenyl ether, and remained unchanged on irradiation of its solution

(Found: C, 80·0; H, 3·6; F, 8·7, 9·0. $C_{28}H_{14}O_2F_2$ requires C, 80·8; H, 3·3; F, 9·0%). The fluorine determination was carried out according to Clark (*Analyt. Chem.*, 1951, **23**, 659), and the estimation of carbon and hydrogen according to Bodenheimer and Goldstein (*Bull. Res. Council Israel*, 1953, **3**, in the press).

4 : 4'-*Dibromodianthron*-9-*yl* (?) (VIII).—1-Bromoanthraquinone (3·0 g.), prepared by cyclisation of 2-benzoyl-3-bromobenzoic acid (von Pechmann, *Ber.*, 1879, **12**, 2123; cf. Bergmann and Loewenthal, *loc. cit.*) with sulphuric acid at 160—180°, was dissolved in concentrated sulphuric acid (45 ml.), and copper powder (3 g.) was added in portions at 25—30°, with stirring. The colour changed slowly from red to greenish-brown. After 0·5 hr., the mixture was slowly heated to 50°, whereupon a yellow precipitate was formed. After 1 hr., the mixture was poured on ice, and the precipitate washed, dried *in vacuo*, and extracted thoroughly with chloroform. The filtered extract was evaporated to a small volume, and boiling ethanol (40 ml.) added. There separated yellowish crystals (1·0 g.), m. p. 235—237° (open capillary). By addition of water to the filtrate, a second crop (1·1 g.) of the same m. p. was obtained. As the m. p. of the product, when determined in an evacuated capillary, was 131—137° (after sintering), the 1-bromoanthrone (VII) which appears to have been formed is evidently oxidized with extreme ease. It could, therefore, not be obtained analytically pure and was dehydrogenated directly with ferric chloride. Thus were obtained 1·75 g. (58%) of the dianthron-9-yl (VIII), m. p. 246—247°. Repeated recrystallization from benzene–ethanol gave pale yellow needles of m. p. 248—249°, which, however, contained less than the theoretical quantity of bromine (Found: Br, 23·0%). Enolized and oxidized in the normal manner, they gave a highly thermochromic (hot xylene) yellow product (m. p. 290—300°); however, the treatment had resulted in loss of most of the bromine (Found: Br, 7·0%).

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## 524. *Allylic Bromination of Unsaturated Terpene Hydrocarbons, and the Synthesis of αβ-Unsaturated Alcohols.*

By A. KILLEN MACBETH, B. MILLIGAN, and J. S. SHANNON.

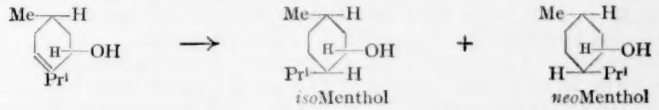
A synthesis of αβ-unsaturated terpene alcohols has been developed, consisting of allylic bromination of unsaturated hydrocarbons by *N*-bromosuccinimide and conversion of the resultant bromides into the alcohols through the formates. (+)-*p*-Menth-3-ene gave (±)-*trans*-*p*-menth-3-en-5-ol, and a (±)-carvotanacetol was obtained from (±)-*p*-menth-1-ene. The yields obtained are inferior to those produced by Treibs and Bast's reaction (*Annalen*, 1948, **561**, 165) using mercuric acetate.

αβ-UNSATURATED terpene alcohols have been prepared conveniently from the unsaturated aldehydes or ketones by reduction by the Ponndorf method, or with lithium aluminium hydride, the latter giving especially good yields. Other methods are required when the parent aldehyde or ketone is not available, and Treibs and Bast (*loc. cit.*) have shown that the reaction of mercuric acetate with an unsaturated terpene hydrocarbon yields the acetate of an αβ-unsaturated alcohol, which is readily hydrolysed. Allylic bromination with *N*-bromosuccinimide (Wohl–Ziegler reaction; *Annalen*, 1942, **551**, 80) has been widely used in steroid chemistry with good results, and the synthesis of an αβ-unsaturated bromide from an unsaturated terpene hydrocarbon for the production of the precursor of an αβ-unsaturated alcohol has now been examined as an alternative to Treibs and Bast's reaction.

Although the bromination by *N*-bromosuccinimide of methylene groups adjacent to unsaturated centres usually gives excellent yields we found that the yields were poor with the two terpene hydrocarbons *p*-menth-1-ene and *p*-menth-3-ene in carbon tetrachloride. Somewhat better yields were obtained in chloroform, and irradiation with ultra-violet light approximately doubled them.

*p*-Menth-3-ene, obtained by the pyrolysis of methyl (−)-menthylxanthate (Malcolm and Read, *J.*, 1939, 1037; Hückel, Tappe, and Legutke, *Annalen*, 1940, **543**, 191) and

repeatedly fractionated over sodium, when irradiated and brominated gave a product which was converted into the alcohol through the formoyloxy-compound (Henbest, *J.*, 1951, 1074). Since *N*-bromosuccinimide effects allylic bromination the resultant alcohol may be the *cis*- or the *trans*-modification of *p*-menth-3-en-2- or -5-ol. Its identity was established as (±)-*trans*-*p*-menth-3-en-5-ol as catalytic hydrogenation under controlled conditions gave a menthol mixture from which the 3 : 5-dinitrobenzoate of (±)-*iso*menthol was isolated. A 2-hydroxy-group is therefore excluded, and the *trans*-configuration of the unsaturated alcohol is indicated by the *iso*menthol relationship :




The isolation of an inactive alcohol from the lævorotatory hydrocarbon is explained by the ready racemisation of *p*-menth-3-ene under acidic conditions (Hückel *et al.*, *loc. cit.*), the succinimide formed in the initial bromination evidently being sufficiently acidic to effect the change.

*p*-Menth-1-ene was initially prepared by the preferential hydrogenation of the exocyclic double bond of limonene at a palladinised charcoal catalyst, but later by an unambiguous synthesis from dihydrocryptone (4-*iso*propyl*cyclo*hexan-1-one) : this was converted by methylmagnesium iodide into 1-methyl-4-*iso*propyl*cyclo*hexan-1-ol which was dehydrated by oxalic acid. The menthene was also derived from (−)-α-phellandrene as the double bond between the two secondary carbon atoms is hydrogenated more readily than that between secondary and tertiary carbon atoms. The yields on bromination were practically the same in all three cases, but only 9% of the 3 : 5-dinitrobenzoate of the alcohol was ultimately obtained. The alcohol may be the *cis*- or the *trans*-form of either (±)-piperitol or (±)-carvotanacetol, the latter being more probable as Treibs and Bast (*loc. cit.*) obtained a carvotanacetol by the reaction of mercuric acetate on *p*-menth-1-ene. As the optically inactive carvotanacetols have not been characterised it was necessary to support the structure of the alcohol by oxidation to (±)-carvotanacetone, which was identified as the semicarbazone. The configuration of the alcohol cannot yet be established as the racemic carvomenthols which are yielded on hydrogenation have not been characterised.

Although much inferior to the Treibs and Bast reaction for the preparation of the unsaturated alcohols, the method may prove of interest for the synthesis of the corresponding amines, acids, and alkyl ethers which are not readily obtainable from the acetate.

## Experimental

p-*Menth*-3-*en*-5-*ol*.—A sample of *p*-menth-3-ene prepared according to Malcolm and Read (*loc. cit.*) and thrice distilled over sodium had b. p. 82—83°/15 mm. and $\alpha_D^{15}$ +44·5° (homogeneous). While being irradiated with ultra-violet light the hydrocarbon (28 g.) in dry chloroform (50 ml.) was gently refluxed with freshly crystallised *N*-bromosuccinimide (22 g.). The initial vigorous exothermic reaction was controlled by external cooling and the mixture was refluxed thereafter for 10 min. Succinimide, filtered off on cooling, was washed with light petroleum (b. p. 40—60°); the combined filtrates were evaporated under reduced pressure, giving crude *p*-menth-3-en-5-yl bromide (36 g., 80% based on *p*-menth-3-ene). The crude bromide (36 g.) in dioxan (50 ml.) was stirred with sodium formate (10 g.) in formic acid (50 ml.; 98%) at room temperature for 2 hr. and after neutralisation (sodium hydrogen carbonate solution) the formate was extracted with ether. The crude *p*-menth-3-en-5-yl formate (30 g.) left on removal of the solvent was hydrolysed overnight with sodium carbonate (8 g.) in aqueous methanol (400 ml.; 50%), and the crude menthenol was extracted with light petroleum (b. p. 40—60°; 4 × 50 ml.). The combined extracts, washed with water (thrice) and dried ($MgSO_4$), were treated with pyridine (5·6 g.) and a solution of 3 : 5-dinitrobenzoyl chloride (16·5 g.) in dry benzene (50 ml.), and the ester was worked up in the usual way and crystallised from light petroleum (b. p. 60—70°), to give colourless needles of (±)-trans-p-*menth*-3-*en*-5-*yl* 3 : 5-*dinitrobenzoate* (5·0 g.), m. p. 142° (Found : C, 58·7; H, 5·75; N, 7·85. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·75; N, 8·05%). Hydrolysis of the ester with methanolic potassium hydroxide (5%) gave (±)-trans-p-*menth*-3-

*en-5-ol*, b. p. 56°/0·7 mm. (Found : C, 77·8; H, 11·8. $C_{10}H_{18}O$ requires C, 77·8; H, 11·75%). The *phenylurethane*, needles from light petroleum, had m. p. 84·5° (Found : C, 74·85; H, 8·25; N, 5·5. $C_{17}H_{23}O_2N$ requires C, 74·7; H, 8·5; N, 5·3%). The *α-naphthylurethane* (needles) had m. p. 109° (Found : C, 77·7; H, 8·1. $C_{21}H_{25}O_2N$ requires C, 78·0; H, 7·8%).

*Hydrogenation of* (±)-p-*Menth-3-en-5-ol.*—The alcohol (0·6 g.) in ethanol (20 ml.) was hydrogenated for 2 hr. at 100°/60 atm. in the presence of Raney nickel (0·4 g.). After filtration and removal of most of the solvent, the oil which separated on dilution of the residue was extracted with light petroleum (b. p. 40—60°), and the extract, washed and dried, was esterified with 3 : 5-dinitrobenzoyl chloride and pyridine. The crude ester (1·1 g., 81%) gave pale yellow needles having m. p. 128° [after three crystallisations from light petroleum (b. p. 40—60°)] alone or mixed with authentic (±)-*iso*menthyl 3 : 5-dinitrobenzoate.

(±)-*Carvotanacetol.*—(±)-*p*-Menth-1-ene was prepared from dihydrocryptone (105 g.) which was added dropwise to an ice-cold solution of a Grignard reagent [from methyl iodide (100 g.) and magnesium (16·8 g.) in ether (550 ml.)] during 4 hr. The mixture was refrigerated overnight and then refluxed for 0·25 hr. After filtration, washing with water, and drying ($MgSO_4$), the crude *p*-menthan-1-ol (105 g., 88%) obtained on removal of the ether was heated under reflux for 3 hr. with oxalic acid (300 g.) in water (600 ml.). Steam-distillation and extraction of the distillate with light petroleum gave a crude hydrocarbon which was fractionated over metallic sodium (yield, 75 g., 86%; b. p. 68—69°/15 mm.). A second sample was obtained by controlled hydrogenation, at room temperature and pressure, of limonene [25 g.; $\alpha_D^{17}$ +56° (homogeneous)] in ethanol (200 ml.) in presence of palladium–charcoal (2 g.; 10%). A third sample was obtained by controlled hydrogenation of α-phellandrene [25 g.; $\alpha_D^{21}$ −73° (homogeneous)] in ethanol (200 ml.) at room temperature and pressure in the presence of platinum oxide (0·25 g.).

*p*-Menth-1-ene (28 g.) in dry chloroform (50 ml.) was brominated with *N*-bromosuccinimide (22 g.) as described above, but the reaction was not as vigorous as in the preceding case and was readily controlled by ceasing irradiation from time to time. The crude bromide (40 g.) was stirred with a solution of sodium formate (10 g.) in formic acid (50 ml.; 98%) for 2 hr., and the crude formate was extracted with ether after neutralisation of the mixture with sodium hydrogen carbonate. The formate (30 g.) was hydrolysed overnight by a solution of sodium carbonate (8 g.) in aqueous methanol (400 ml.; 50%), and the carvotanacetol formed was extracted with light petroleum (b. p. 40—60°). After being washed and dried the extract was treated with 3 : 5-dinitrobenzoyl chloride and pyridine, and the crude dinitrobenzoate remaining after distillation with steam was recrystallised (four times) from light petroleum (b. p. 40—60°), to give (±)-*carvotanacetol* 3 : 5-*dinitrobenzoate* as needles, m. p. 94·5° (Found : C, 58·8; H, 5·85; N, 7·8. $C_{17}H_{20}O_6N_2$ requires C, 58·6; H, 5·75; N, 8·0%). The yield of ester was less than 9% based on the crude bromide used.

The dinitrobenzoate (1·8 g.) in ether (30 ml.) was hydrolysed under reflux for 10 min. with potassium hydroxide (1 g.) in methanol (10 ml.). After 1 hr. filtration and removal of most of the solvent gave an oil. This was washed in light petroleum with water and dried, and gave crude (±)-carvotanacetol (0·8 g.). The alcohol (0·8 g.) in acetic acid (15 ml.) containing chromium trioxide (0·5 g.) was kept at 35° for 1 hr. The oil which separated on dilution was extracted with light petroleum (four times), and after being washed with 5% sodium carbonate solution and then water, and dried, gave the crude ketone (0·3 g.). This was converted into the semicarbazone which twice recrystallised had m. p. 175° alone or mixed with authentic (±)-carvotanacetone semicarbazone.

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## 525. *The Detection and Determination of "End Groups" in O-Methylcelluloses.*

By D. I. McGilvray.

Tetra-*O*-methylglucose end groups have been detected and determined in hydrolysates of *O*-methylcelluloses. Degrees of polymerisation have been calculated from physico-chemical data and from end-group contents. To minimise degradation during methylation oxygen must be very rigorously excluded. The presence of end groups has been demonstrated in *O*-methylcelluloses soluble in chloroform–light petroleum (1 : 1) of degree of polymerisation about 1000 and in derivatives insoluble in this solvent and of greater chain length. This evidence is contrary to that upon which Haworth (*Chem. and Ind.*, 1939, **17**, 917) formulated his theory of the behaviour of cellulose during methylation. The results do not exclude the possibility that the original cellulose might be branched to a slight extent. With the rigorous exclusion of oxygen during the methylation a high percentage of the product is insoluble in the chloroform–light petroleum solvent. These insoluble materials, although possessed of end groups, do not, on analysis, yield evidence which would provide a sound basis for conclusions as to the structure of the original molecule.

Naturally occurring celluloses have long been recognised as polysaccharides composed almost entirely of D-glucose residues, but knowledge of the finer structural features of the molecule remains incomplete. The terminal non-reducing residue of a polyanhydroglucose chain will, after methylation and hydrolysis, give rise to tetra-*O*-methylglucose and the presence of this sugar has been demonstrated in hydrolysates of methylated cotton celluloses (Haworth, Hirst, Owen, Peat, and Averill, *J.*, 1939, 1885; Haworth, Montanna, and Peat, *ibid.*, p. 1899; Hess, Grigorescue, Steurer, and Frahm, *Ber.*, 1940, **73**, 669). In the case of an unbranched long-chain molecule determination of the tetra-*O*-methylglucose will give a value for the number average degree of polymerisation, but the method used by Hess *et al.* for this analysis (Neumann and Hess, *Ber.*, 1937, **70**, 721; Leckzyck, *ibid.*, 1938, **71**, 829) has been shown to be unreliable (Averill and Peat, *J.*, 1938, 1244; Hirst and Young, *ibid.*, p. 1247). Haworth and his co-workers found that if the methylation was carried out in the presence of oxygen the cellulose was degraded and end groups were determined in amounts to agree with physico-chemically estimated degrees of polymerisation; on the other hand they reported that if oxygen was excluded during the methylation the cellulose was degraded as before but no end groups could be detected after hydrolysis. On the basis of these results Haworth put forward a theory (*Chem. and Ind.*, 1939, **17**, 917) of the re-combination of reducing and non-reducing end groups to give ring structures in the absence of oxygen, this linking being prevented if oxygen was present and made possible by some unspecified type of bridge which held the cellulose chains in positions favourable for ring closure. This problem has now been re-examined, paper-chromatographic analysis being used for the separation of the end group before its determination.

In order to minimise degradation unscoured cotton was used as the raw material for most of these experiments. The procedure was essentially as described by Haworth *et al.* (*loc. cit.*) except that the methylation liquors were neutralised with sulphuric acid while still under nitrogen. Degrees of polymerisation were calculated from viscosity data and in some cases from osmotic pressures. These determinations on natural cellulose were carried out on the trinitrate prepared under anhydrous conditions and dissolved in butyl acetate, and those on the soluble *O*-methylcelluloses in chloroform. It was found that 90% formic acid hydrolysed *O*-methylcellulose much faster and under less drastic conditions than the methods which had been used by previous workers. When pure 2 : 3 : 6-tri-*O*-methylglucose was subjected to this hydrolytic procedure, no demethylation was observed.

Dewaxed American cotton was methylated in an atmosphere of pyrogallol-washed nitrogen (Expt. 1). The dried *O*-methylcellulose was extracted with chloroform, giving a

very viscous solution containing undissolved material. In order to separate on the centrifuge the soluble from the insoluble *O*-methylcellulose it was necessary to reduce the viscosity of the chloroform extract by the addition of an approximately equal volume of light petroleum. That fraction which then remained in solution was used for the end-group determination. To cause its precipitation it was necessary to add a further four volumes of light petroleum. It is the first solvent, chloroform–light petroleum (1 : 1), which is implied when *O*-methylcelluloses are referred to below as soluble or insoluble. Measurement of the viscosity of this soluble *O*-methylcellulose in chloroform showed that extensive degradation had accompanied the methylation. After hydrolysis and methyl glucoside formation any methyl tetra-*O*-methylglucoside present was concentrated by extraction of an aqueous solution of the glucosides with purified light petroleum (Brown and Jones, *J.*, 1947, 1344). These extracts were hydrolysed and the neutralised hydrolysates examined on a paper chromatogram. Two components were detected, the faster of which travelled with 2 : 3 : 4 : 6-tetra- and the other with 2 : 3 : 6-tri-*O*-methylglucose in the two solvent systems used. The ratio of tetra- to tri-*O*-methylglucose was determined by buffered sodium hypoiodite (Chanda, Hirst, Jones, and Percival, *J.*, 1950, 1294) after separation of the two sugars by paper chromatography with ethyl methyl ketone as solvent.

In the second experiment bleached wood pulp was methylated in nitrogen and the soluble portion of the product subjected to an end-group analysis as described before. Degradation had again occurred during methylation. The details of these two experiments are summarised in Table 1.

TABLE 1.

| | | Natural cellulose: D.P. calc. from | | | | *O*-Methylcellulose: D.P. calc. from | | |
|---|---|---|---|---|---|---|---|---|
| Expt. no. | Source | viscosity | osmotic press. | Sol. in chloroform–petroleum (%) | OMe (%) | viscosity | osmotic press. | end group |
| 1 | American Cotton | 3900 | 2200 | 75 | 43·7 | 256 | — | 245 |
| 2 | Bleached Wood Pulp | 800 | — | 84 | 43·1 | 260 | 200 | 244 |

(D.P. = degree of polymerisation.)

The sugars isolated from the *O*-methylcellulose hydrolysates were proved to be 2 : 3 : 4 : 6-tetra- and 2 : 3 : 6-tri-*O*-methylglucose by comparison of the infra-red spectrum of an end-group concentrate from a further sample of *O*-methylcellulose with the spectra of known specimens. The reliability of the concentration and analytical method for the determination of the end group was tested by the analysis of a synthetic 1 : 1500 mixture of tetra- and tri-*O*-methylglucose; four paper-chromatographic determinations gave an average value within 6% of the theoretical.

It is considered that these two experiments simulated those reported by Haworth *et al.* (*loc. cit*) for the methylation of cellulose under "oxygen-free" conditions. They confirm the degradation under those conditions. No difficulty was experienced, however, in detection and determination of the tetra-*O*-methylglucose, and the values they afford for the degrees of polymerisation agree with those values obtained physico-chemically. Thus there is no evidence in these experiments for linking of end groups in the absence of oxygen.

In order to reduce the degradation, dewaxed Egyptian cotton was methylated under two sets of conditions (Expts. 3—4 and 5—6), the second set being more efficient than the first in exclusion of oxygen. Experiment No. 6 was the most carefully conducted of the series. Parallel with this exclusion of oxygen the percentage of the resulting *O*-methylcelluloses which was soluble in chloroform–light petroleum (1 : 1) diminished. These soluble materials were hydrolysed and the end groups which were detected in the hydrolysates were determined, giving values for the degrees of polymerisation. The results obtained in experiments 3—5 are shown in Table 2.

The discrepancy between the values for the number average degrees of polymerisation obtained by osmotic and end-group measurements may be expained by assuming a slightly branched structure for these soluble *O*-methyl celluloses. The maximum permissible number of branches (about one per cellulose molecule) is, however, sufficiently small to

require further evidence for substantiation. It is considered that the errors inherent in the classical methylation technique render it incapable of providing a final decision on this point.

The soluble *O*-methylcelluloses prepared under increasingly oxygen-free conditions are seen to be less and less degraded, in accord with the well-established degradation of cellulose in the presence of alkali and oxygen. From a consideration of the degrees of polymerisation

TABLE 2. *Natural cellulose: Egyptian cotton, D.P. (viscosity) 4600, D.P. (osmotic) 2300.*

| | *O*-Methylcellulose | | | | |
|---|---|---|---|---|---|
| | | | Degree of polymerisation calc. from | | |
| Expt. no. | Product. sol. in chloroform–petroleum (%) | OMe (%) | viscosity | osmotic press. | end groups |
| 3 | 50 | 44·0 | 890 | 610 | 495 |
| 4 | 64 | 42·5 | 850 | 720 | 540 |
| 5 | 47 | 42·7 | 1250 | 1050 | 880 |

of the *O*-methylcelluloses in the range 1000—200, as determined by the physico-chemical and end-group methods, it may be concluded that each break in the cellulose chain gives rise to one non-reducing end group. These may be formed either by direct action on a β-glucosidic linkage or by the oxidation of one or more glucose residues producing in the molecule linkages which are labile to alkaline hydrolysis, the oxidised residues themselves then being completely broken down.

A high proportion of the *O*-methylcelluloses prepared in experiments 3—6 is insoluble, increasingly as the precautions to exclude oxygen are increased. Indeed in experiment 6 the *O*-methylcellulose contained 39·5% of methoxyl, and 75% of the material was insoluble. These insoluble fractions were hydrolysed and the presence of end groups in the hydrolysates demonstrated. Determination of the end group is the only method of assessing the degree of polymerisation in this instance, but the values will tend to be high owing to the under-methylation. The degrees of polymerisation are of the same order as that of the starting material (Table 3).

TABLE 3.

| Sample no. | No. of methylations | Product insol. in chloroform–petroleum (%) | OMe (%) | D.P. (end group) |
|---|---|---|---|---|
| 6*a* | 6 | 77 | 38·1 | 2340 |
| 6*b* | 7 | 74 | 37·9 | 2040 |

The conditions under which these two samples of *O*-methylcellulose were prepared are considered to be essentially non-degradative and the detection of end groups in the hydrolysates indicates that the original cellulose molecule had an open-chain and possibly an unbranched structure.

As degradation during the methylation is minimised by the exclusion of oxygen the amount of insoluble fraction increases. No valid conclusions as to the structure of the original cellulose molecule can be drawn if this very significant fraction is neglected. These insoluble materials however, by virtue of their under-methylation, are unsuitable for use in the determination of the fine details of molecular stucture. These results are included therefore to show the limitations in the method.

Paper chromatography and ionophoresis (Foster, *Chem. and Ind.*, 1952, 828, 1050; Foster and Stacey, *J. Appl. Chem.*, 1952, **3**, 19) of the constituents of these insoluble *O*-methylcellulose hydrolysates has shown the virtual absence of 3-*O*-methyl- and 3 : 6-di-*O*-methyl-glucose and the presence of all the other possible isomers. The possibility thus arises that in a proportion of the glucose residues in the cellulose positions 3 and 6 may be prevented from reacting under these conditions of methylation, for reasons which are being studied further.

## EXPERIMENTAL

The cotton, in the form of card sliver, was de-waxed by extraction (Soxhlet) with ethanol for 17 hr., followed by ether for 12 hr., and was dried at 50°. It was then milled in a Raymond Laboratory Mill to a staple length of 1—2 mm. The ethanol extracts, after filtration and evapor-

ation, were shown by paper chromatography to contain mannose, glucose, and galactose, together with cellobiose and higher oligosaccharides (see also Guthrie and Reeves, *Textile Res. J.*, 1950, **20**, 859). Two solvent systems were used for the paper chromatography: Ethyl methyl ketone, 10% undersaturated with water; and the organic layer of a butanol–ethanol–water (4 : 1 : 5) (approx. 10% undersaturated with water). Undersaturation was to prevent streaking of the chromatograms by the separation of water from the organic solvent should the temperature fall overnight. *p*-Anisidine hydrochloride (Hough, Jones, and Wadman, *J.*, 1950, 1702) was used as spray. Evaporations were carried out at 40°/15 mm., unless otherwise stated. The nitrogen used was British Oxygen Co. "oxygen free," said to contain less than 10 p.p.m. oxygen.

*Molecular-weight Measurements.*—The osmometer was of a modified Fuoss–Mead type, with a vertical membrane, and kept at 25·0° ± 0·002°. Membranes were prepared from never-dried Cellophane (British Cellophane Ltd., 300 gel film). The viscometer was of the capillary type, kept at 25·0° ± 0·05°, and so designed that the corrections for non-laminar flow were negligible.

*Natural Cellulose.*—The trinitrate was prepared under anhydrous conditions (Sharples, unpublished work). Osmotic pressure determinations were made on its solution in acetone and corrected for the density effect (Higginbotham, *J. Text. Inst.*, 1951, **42**, T235). The error at this degree of polymerisation was *ca.* 10%. The viscosity determinations were carried out on butyl acetate solutions and the results were corrected for rate of shear and converted into degrees of polymerisation by D.P. = $92{\cdot}5\eta$ (Harland, unpublished results).

*O-Methylcellulose in Chloroform Solution.*—Osmotic results were corrected for the density effect. The viscosity results were not corrected for rate of shear. At D.P. (visc.) = 2000 the values could be 5% low; this error at D.P. (visc.) = 1000 would be negligible. Intrinsic viscosities were converted to degrees of polymerisation by D.P. = $91\eta$ (Staudinger and Reinecke, *Annalen*, 1938, **535**, 47).

*Experiment No.* 1.—Milled, de-waxed American cotton (20 g.) was suspended in sodium hydroxide solution (1500 ml.; 30%) with rapid stirring, under nitrogen previously washed with alkaline pyrogallol solution. After 2 hr., methyl sulphate (275 ml.) in dioxan (275 ml.) was added dropwise, at approx. 40°; the current of nitrogen and agitation were continued overnight. The temperature was lowered to 0° and the alkali neutralised by sulphuric acid (50%), the nitrogen atmosphere and the stirring being maintained meanwhile. The insoluble partially methylated cotton was separated from the neutral liquors by filtration on sintered glass, and washed with hot water to remove the majority of the inorganic material.

Repetition of this process 4 times yielded crude *O*-methylcellulose (22 g.) (Found: OMe, 41·3%). The cotton was not allowed to dry between the methylations. The methoxyl content could not be increased by further treatment with the methylating reagents.

The crude material was dried (50°) and shaken with chloroform (1 l.). The resulting viscous suspension was diluted with light petroleum (b. p. 40—60°; 1 l.), and the highly swollen solid (fraction 1) separated centrifugally from the clear viscous solution. It was then triturated with light petroleum until free from chloroform and dried (50°) (5·4 g.) (Found: OMe, 39·6%). Fraction 2 was obtained from the centrifugate by complete precipitation with light petroleum. It was triturated and dried as above (15·7 g.), viscosity average D.P. 256 (Found: OMe, 43·7%).

*Hydrolysis of methylated cellulose.* Fraction 2 (8·0 g.) was treated with formic acid (170 ml.; 90%) on a boiling-water bath until the rotation was constant (5 hr.). The acid was removed by evaporation, and water (3 × *ca.* 100 ml.) was added, with evaporation between additions. The product was dried by distillation of its solution in ethanol–benzene, to leave a syrup (8·65 g.) which readily crystallised. These free sugars were refluxed with methanolic hydrogen chloride (200 ml.; 2—3%) for 16 hr. and after working up in the usual way the glucosides were obtained as a clear syrup (9·1 g.).

*Partial fractionation of the methyl glucosides by solvent extraction.* The glucosides were dissolved in water (80 ml.) and divided into two portions, each of which was extracted for 2 periods of 3 hr. with light petroleum (b. p. 38—41°) in a liquid–liquid extraction apparatus (Brown and Jones, *loc. cit.*). The corresponding extracts (fractions 1 and 2) from each portion were combined and the solvent evaporated with very slight reduction in pressure, giving from fraction 1 0·5148 g., and from fraction 2 0·4955 g.

*Hydrolysis of petroleum extracts and paper chromatography.* Hydrolysis of the petroleum-soluble glucosides was effected by treatment with sulphuric acid (50 ml.; 2N) on a boiling-water bath for 16 hr. Neutralisation with barium carbonate, filtration, washing of the solids, and evaporation gave the free sugars (fractions 1*a* and 2*a*) which readily crystallised *in vacuo* over phosphoric oxide (fraction 1*a* 0·4751 g.; fraction 2*a* 0·4504 g.). These materials were treated

in water (5 ml.) with a little "Deminrolite" ion-exchange resin (Permutit Co. Ltd.) before chromatography. Each fraction contained only two components: the faster travelled with 2 : 3 : 4 : 6-tetra- and the other with 2 : 3 : 6-tri-*O*-methylglucose in both the solvent systems used. $R_G$ values for the ethyl methyl ketone system, the solvent front having travelled 90—100 cm. in 12 hr. at 20°, were: 2 : 3 : 4 : 6-tetra-*O*-methylglucose 1·00; 2 : 3 : 4 : 6-tetra-*O*-methylmannose 0·97; 2 : 3 : 6-tri-*O*-methylglucose 0·75; 2 : 3 : 4 : 6-tetra-*O*-methylgalactose 0·85.

The ratio of tetra- to tri-*O*-methylglucose in the above fractions was determined by hypoiodite oxidation (Chanda, Hirst, Jones, and Percival, *loc. cit.*). The sugars were washed from the relevant portions of the chromatogram with cold distilled water (5 ml.) dropping slowly from burettes through the paper into B.24 boiling-tubes. 0·1N-Iodine (1 ml.) was added from a 1-ml. pipette, with a standardised technique, being followed by buffer solution (3 ml.; pH 11·4). The stoppers were sealed with potassium iodide solution (10%), and the tubes kept in the dark for 3 hr. After acidification with sulphuric acid (3 ml.; 2N) the liberated iodine was titrated against *ca.* 0·01N-sodium thiosulphate. Paper blank determinations were run concurrently. The differences between these two titrations gave the required ratio. The value of this ratio for each fraction was derived from at least four paper-chromatographic estimations. Ratios of tetra- to tri-*O*-methyl sugars were 1 : 16·0 in fraction 1*a* and 1 : 51·7 in fraction 2*a*. Light petroleum thus extracted 38·4 mg. of tetra-*O*-methylglucose (0·163 millimole of tetra-*O*-methylanhydroglucose); 8·0 g. of tri-*O*-methylcellulose is equiv. to 39·21 millimoles of tri-*O*-methylanhydroglucose, whence D.P. by end-group estimation = 245.

*Experiment No.* 2.—A sample (20 g.) of a bleached wood pulp (viscosity average D.P. 800) was treated as described above. The results are shown in Table 1.

*Determination of Tetra-O-methylglucose in a Known Mixture by the Above Method.*—Pure distilled methyl 2 : 3 : 4 : 6-tetra- (3·524 mg.) and distilled methyl 2 : 3 : 6-tri-*O*-methyl-α-D-glucoside (5·2861 g.) in water (50 ml.) were analysed as above, 3·74 mg. (106%) of tetra-*O*-methylglucose being recovered.

*Determination of the Extent of Demethylation during Hydrolysis.*—Chromatographically pure 2 : 3 : 6-tri-*O*-methylglucose (1·0 g.) was hydrolysed as was the *O*-methylcellulose. The crystalline material recovered (0·955 g.) was analysed on the paper chromatogram and found to contain only 2 : 3 : 6-tri-*O*-methylglucose.

*Infra-red Spectra.*—These were taken on a Sir Howard Grubb, Parsons S3 sepctrometer fitted with a rock-salt prism. The spectrum of 2 : 3 : 6-tri-*O*-methylglucose was recorded for its solution in dry chloroform; the 2 : 3 : 4 : 6-tetra-*O*-methylglucose was dissolved in dry carbon tetrachloride, as was the end-group concentrate. This concentrate was obtained by ether-extraction of an aqueous solution of the free sugars produced on hydrolysis of a further sample of *O*-methylcellulose prepared under the conditions used in Experiments 1 and 2 and after removal of any formyl esters by hydrolysis by dilute sulphuric acid.

*Methylations under more rigorously Controlled Conditions.*—Egyptian cotton (Sudan Sakel, type G.3.L.) was used in these experiments. The reactions were carried out in the dark with the quantities of reagents used in experiment 1. The results are given in Tables 2 and 3.

*Experiment No.* 3.—The sodium hydroxide solution was saturated whilst hot with nitrogen, previously washed by passage through a train of bottles fitted with sintered-glass bubblers containing an alkaline solution of sodium anthraquinone-2-sulphonate (Whelan and Peat, *J. Soc. Dyers and Col.* 1949, **65**, 756). The dioxan and methyl sulphate were distilled off under nitrogen, the latter under reduced pressure, and subsequently stored under nitrogen. The nitrogen entering the reaction flask was also washed by the above solution. Milled de-waxed cotton (20 g.) after four methylations yielded a crude granular methyl derivative (22·4 g.) (Found: OMe, 41·6%). A portion (10 g.) of the soluble fraction (11·2 g.) (Found: OMe, 44·0%) was hydrolysed and the end groups which were detected in the hydrolysate were determined, giving a value for the number average degree of polymerisation of this methylcellulose.

*Experiment No.* 4.—The same precautions were observed for the exclusion of oxygen as in experiment 3. Cotton (20 g.) after four methylations gave a granular methyl derivative (22·3 g.) (Found: OMe, 41·7%). This was fractionated as before and a portion (11·5 g.) of the soluble material (13·5 g.) (Found: OMe, 42·5%) analysed for end groups.

*Experiment No.* 5.—In addition to the above precautions to exclude oxygen, the flask containing the milled cotton was evacuated and filled with washed nitrogen four times before each methylation. Cotton (20 g.) after five methylations gave a granular methyl derivative (23·5 g.) (Found: OMe, 41·5%) which was fractionated as above. The soluble methylcellulose (9·2 g.) (Found: OMe, 42·7%) was hydrolysed and analysed for end groups.

*Experiment No.* 6.—The above precautions for the exclusion of oxygen during the methylation were applied as rigorously as possible. Cotton (20 g.) was subjected to six methylations, and the still fibrous material (21 g.) (Found : OMe, 39·5%) was divided into two portions (samples **6***a* and **6***b*) one of which (**6***b*; 10 g.) was remethylated. It remained fibrous and of the same methoxyl content. Both samples were fractionated as before. End groups were present in the hydrolysates of the soluble and the insoluble fractions, but the weights of the soluble materials (from **6***a* : 2·3 g.; 23%; OMe, 43·0%. From **6***b* : 2·4 g.; 26%; OMe, 42·9%) were too small to permit accurate determination of the end group. The insoluble materials (from **6***a*; 7·7 g.; OMe, 38·1%. From **6***b* : 6·9 g.; OMe, 37·9%) were subjected to end-group assay.

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## 526. *Alicyclic Glycols. Part XII.* Derivatives of* cyclo*Heptane*-1 : 2-*diol.*

By L. N. Owen and G. S. Saharia.

Some monoesters, simple diesters, and mixed diesters of *cis*- and of *trans*-*cyclo*heptane-1 : 2-diol have been prepared. *trans*-2-Chloro-, -2-bromo-, and -2-iodo-*cyclo*heptanol are obtained by fission of *cyclo*heptene oxide with the corresponding hydrogen halide and also by reaction of the monotoluene-*p*-sulphonate of the *trans*-diol with lithium chloride, lithium bromide, and sodium iodide, respectively; a *trans*-halogenohydrin is also obtained by reaction of the monotoluene-*p*-sulphonate of the *cis*-diol with the appropriate metal salt. With calcium carbonate and aqueous acetone, *trans*-2-acetoxy-*cyclo*heptyl toluene-*p*-sulphonate gives *cis*-2-acetoxy*cyclo*heptanol; an ethyl ether, also, is formed when ethanol is the solvent. The *trans*-monotoluene-*p*-sulphonate reacts with alkali much more rapidly than does the *cis*-isomer; the products are *cyclo*heptene oxide and *cyclo*heptanone, respectively. Comparison with the corresponding *cyclo*pentane and *cyclo*hexane derivatives shows that for the *cis*- and for the *trans*-monotoluene-*p*-sulphonates of the 1 : 2-diols the order of reactivity towards alkali is *cyclo*pentane > *cyclo*heptane > *cyclo*hexane.

The *cis*- and the *trans*-form of *cyclo*heptane-1 : 2-diol were first prepared by Böeseken and Derx (*Rec. Trav. chim.*, 1921, **40**, 529; Derx, *ibid.*, 1922, **41**, 312), the *cis* being obtained in poor yield by hydroxylation of *cyclo*heptene with buffered aqueous permanganate, and the *trans* by acid hydrolysis of *cyclo*heptene oxide; support for the configuration of the *trans*-diol was provided by Godchot and Mousseron (*Compt. rend.*, 1934, **198**, 837; **199**, 1233; *Bull. Soc. chim.*, 1946, 643) who obtained from it a pair of diastereoisomeric strychnine sulphates. In marked contrast to the *cyclo*pentane- and *cyclo*hexane-1 : 2-diols, both stereoisomers of *cyclo*heptane-1 : 2-diol yield *iso*propylidene derivatives and augment the conductivity of boric acid (Böeseken and Derx, *loc. cit.*; Derx, *loc. cit.*; Böeseken, *Rec. Trav. chim.*, 1939, **58**, 856). Both stereoisomers are formed by reduction of tropolone (Cook, Gibb, Raphael, and Somerville, *Chem. and Ind.*, 1950, 427; Doering and Knox, *J. Amer. Chem. Soc.*, 1951, **73**, 836).

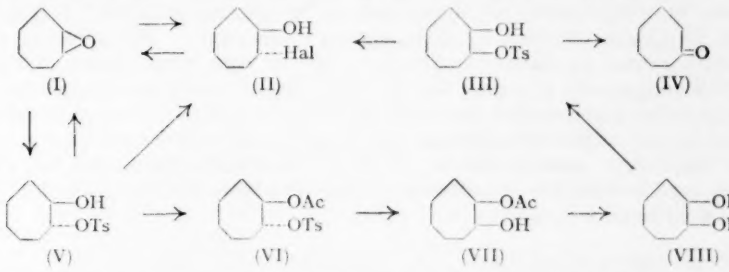
For the present investigation, the *cis*-diol was prepared by Derx's method (*loc. cit.*), and the yield was improved to 35% by carrying out the hydroxylation at −40°. Very

* Part XI, Haggis and Owen, *J.*, 1953, 408.

poor yields of *cis*-diol were obtained by hydroxylation of *cyclo*heptene, in the presence of osmic acid, with either hydrogen peroxide in *tert.*-butanol (cf. Milas and Sussman, *J. Amer. Chem. Soc.*, 1936, **58**, 1302) or aqueous sodium chlorate (cf. Milas and Terry, *ibid.*, 1925, **47**, 1412; Milas, *ibid.*, 1927, **49**, 2005); towards these reagents *cyclo*heptene thus behaves like *cyclo*pentene and unlike *cyclo*hexene (cf. Owen and Smith, *J.*, 1952, 4026). The *trans*-diol was obtained in 53% yield by hydroxylation of *cyclo*heptene with performic acid. Each stereoisomer was characterised as the crystalline bis-3 : 5-dinitrobenzoate, dimethanesulphonate, and ditoluene-*p*-sulphonate.

Monohalides (II) were synthesised by ring-fission of *cyclo*heptene oxide (I) with the appropriate hydrogen halide in ether, and the resulting *trans*-2-chloro-, -2-bromo-, and -2-iodo-*cyclo*heptanol were each characterised as crystalline 3 : 5-dinitrobenzoate; each halogenohydrin gave the oxide (I) when warmed with aqueous alkali. Reaction of the oxide with acetic acid, with toluene-*p*-sulphonic acid, and with methanesulphonic acid gave respectively the *trans*-monoacetate, the *trans*-monotoluene-*p*-sulphonate (V), and the *trans*-monomethanesulphonate, which were characterised as the following mixed esters: *trans*-acetate 3 : 5-dinitrobenzoate, *trans*-methanesulphonate 3 : 5-dinitrobenzoate, *trans*-methanesulphonate toluene-*p*-sulphonate (obtained from the monomethanesulphonate and from the monotoluene-*p*-sulphonate), and the *trans*-benzoate toluene-*p*-sulphonate.

In studies on the *cyclo*hexane-1 : 2-diols (Clarke and Owen, *J.*, 1949, 315) and *cyclo*pentane-1 : 2-diols (Owen and Smith, *loc. cit.*) the *cis*-monoacetates were obtained by reaction of the appropriate *trans*-acetate toluene-*p*-sulphonate with ethanol and calcium carbonate or potassium acetate, according to the general method of Winstein and Buckles (*J. Amer. Chem. Soc.*, 1942, **64**, 2780; Winstein, Hess, and Buckles, *ibid.*, p. 2796). When this method was applied to the acetate toluene-*p*-sulphonate (VI) of *trans-cyclo*heptane-1 : 2-diol, a pure monoacetate could not be isolated, the product being contaminated with an ethoxy-containing material presumably formed by alcoholysis of the toluene-*p*-sulphonyloxy-group; this type of side reaction has apparently not previously been observed under these conditions. However, by carrying out the reaction with calcium carbonate in aqueous acetone, instead of ethanol, the pure *cis*-monoacetate (VII) was obtained; its




configuration was confirmed by hydrolysis to the *cis*-diol (VIII). Toluene-*p*-sulphonylation of the *cis*-monoacetate gave the *cis*-acetate toluene-*p*-sulphonate, but attempts to convert this into the *cis*-monotoluene-*p*-sulphonate, by preferential alcoholysis of the acetate residue with methanolic hydrogen chloride, were unsuccessful. The *cis*-monotoluene-*p*-sulphonate (III) was therefore prepared by partial toluene-*p*-sulphonylation of the *cis*-diol under mild conditions; it was characterised as the crystalline *cis*-benzoate toluene-*p*-sulphonate.

Reactions of the monotoluene-*p*-sulphonates with metallic salts, and with alkali, were carried out so that comparison could be made with the corresponding reactions in the *cyclo*hexane and *cyclo*pentane series (Clarke and Owen, *loc. cit.*; Owen and Smith, *loc. cit.*). With lithium chloride, lithium bromide, and sodium iodide, the *trans*-ester (V) gave the respective *trans*-halogenohydrin (II), identified in each case as the 3 : 5-dinitrobenzoate, identical with that already obtained from the halogenohydrin prepared from the oxide. The *trans*-chlorohydrin was also obtained by reaction of the *cis*-monotoluene-*p*-sulphonate (III) with lithium chloride, and the *trans*-bromohydrin by reaction of the

*cis*-acetate toluene-*p*-sulphonate with lithium bromide, followed by acid hydrolysis of the resulting *trans*-bromide acetate. The overall retention of configuration in replacement of the *trans*-toluene-*p*-sulphonyloxy-group, and inversion in replacement of the *cis*-group, is thus similar to that observed with the five- and six-membered rings, and can be explained by similar mechanisms.

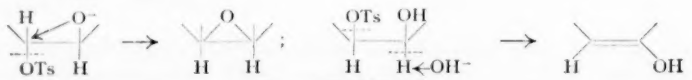
With alkali, the *trans*-monotoluene-*p*-sulphonate readily gave *cyclo*heptene oxide, whereas the *cis*-isomer reacted more slowly and gave *cyclo*heptanone (IV). This behaviour, also, corresponds to that in the smaller ring-systems, and indicates that the *cyclo*heptane ring is not sufficiently flexible to allow of the easy formation of a *trans*-1 : 2-oxide; with larger rings, *e.g.*, *cyclo*decane, both a *cis*- and a *trans*-1 : 2-oxide can be obtained by reaction of the *cis*- and the *trans*-*cyclo*olefin, respectively, with perbenzoic acid (Prelog, Schenker, and Günthard, *Helv. Chim. Acta*, 1952, **35**, 1598), and each oxide would probably be formed also from the monotoluene-*p*-sulphonate of the 1 : 2-diol of opposite configuration.*

Quantitative experiments were carried out to determine the rates of reaction of the monotoluene-*p*-sulphonates (III) and (V) with methanolic potassium hydroxide at 20°, and the reaction of the monotoluene-*p*-sulphonate of *trans*-*cyclo*hexane-1 : 2-diol, previously recorded by Clarke and Owen (*loc. cit.*) at 17°, was repeated at 20° by the modified technique. Approximate second-order velocity constants at 20°, calculated from the data given in the present and the earlier papers, are recorded below.

*Reactions of the* ***monotoluene***-p-*sulphonates of* cyclo*alkane*-1 : 2-*diols with methanolic potassium hydroxide at* 20°.

| Ring size | 5 | | 6 | | 7 | |
|---|---|---|---|---|---|---|
| | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* |
| $k_2$ (mole l.$^{-1}$ min.$^{-1}$) ..... | 0·17 | 140 | 0·005 (17°) | 15 | 0·018 | 25 |

The absolute values of the rate constants are dependent upon the composition of the solvent (see, *e.g.*, Owen and Smith, *loc. cit.*), and may therefore be slightly affected by variation in the water-content of the methanolic alkali used on different occasions. Furthermore, in several cases they diminished as the reaction proceeded, and the values quoted are then those obtained by extrapolation to zero time. Nevertheless, although great accuracy cannot be claimed (particularly for the high rates encountered with the more reactive compounds) it is clear that for each ring-size the *trans*-compound is several hundred times more reactive than the *cis*-isomer; for the former the rate-determining step is the attack by the neighbouring anionic oxygen on the carbon atom carrying the toluene-*p*-sulphonyloxy-group, accompanied by fission of the C–OTs bond, and this evidently occurs more readily than the elimination reaction undergone by the *cis*-isomer, in which fission of a C–H bond is involved :




(Ts = *p*-$C_6H_4Me{\cdot}SO_2$)

It is significant that the *cis*-monotoluene-*p*-sulphonates give the ketones, and not the 2-en-1-ols; elimination thus occurs towards the CH(OH) rather than the $CH_2$ group, probably because the hydroxyl group ($-I$ effect) weakens the C–H bond of the carbon atom to which it is attached, thus favouring attack by $OH^-$ (or $OMe^-$) at that position.

Brown and Borkowski (*J. Amer. Chem. Soc.*, 1952, **74**, 1894; cf. Brown, Fletcher, and Johannesen, *ibid.*, 1951, **73**, 212) have measured the rates of solvolysis of various 1-methyl-*cyclo*alkyl chlorides and report the values $k_1$ = 1·32, 0·0106, and 1·15 hr.$^{-1}$ at 25° for the five-, six-, and seven-membered rings, respectively. The greater reactivity of certain other *cyclo*pentane and *cyclo*heptane compounds, compared with the corresponding *cyclo*-

* Mousseron's claim (*Bull. Soc. chim.*, 1946, 629) to have obtained *trans*-*cyclo*pentene oxide is not supported by adequate experimental evidence, and his views on the stereochemistry of oxide formation and oxide fission cannot be accepted.

hexane derivatives, was previously emphasised by Prelog (*J.*, 1950, 420). The present results are thus in general agreement with expectation, although the very high reactivities of the monotoluene-*p*-sulphonates of *cyclo*pentane-1 : 2-diol are not encountered with the *cyclo*heptane compounds. Strict comparison with the halides is, however, not justifiable, because the reactions undergone by the monotoluene-*p*-sulphonates are of the $S_N2$ and $E2$ types, and would clearly be subject to different steric factors from those operating in the $S_N1$ and $E1$ reactions of the halides.

## Experimental

Hydrogenation of *cyclo*heptanone in alcohol, over Raney nickel at 150°/120 atm., gave *cyclo*heptanol, b. p. 95°/35 mm., $n_D^{19}$ 1·4760, in almost quantitative yield. The 3 : 5-*dinitrobenzoate* crystallised from aqueous ethanol in needles, m. p. 79° (Found : C, 54·5; H, 5·3; N, 9·3. $C_{14}H_{16}O_6N_2$ requires C, 54·5; H, 5·2; N, 9·1%).

Dehydration of *cyclo*heptanol by distillation over naphthalene-β-sulphonic acid (Kohler, Tishler, Potter, and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 1057) or phosphoric acid (Dehn and Jackson, *ibid.*, 1933, **55**, 4284) gave *cyclo*heptene (in *ca.* 70% yield), b. p. 112—113°, $n_D^{20}$ 1·4580.

trans-cyclo*Heptane*-1 : 2-*diol*.—A mixture of formic acid (560 g.) and 30% aqueous hydrogen peroxide (73 g.) was slowly added to *cyclo*heptene (24 g.), the temperature being kept below 45° during the addition, and at 45—50° for a further 4 hr. The homogeneous solution was then concentrated under reduced pressure to remove formic acid, and the residue was boiled under reflux for 1·5 hr. with 10% aqueous sodium hydroxide (390 c.c.). The solution was neutralised with hydrochloric acid and evaporated to dryness; extraction of the residue with boiling chloroform gave the *trans*-diol, which was purified by distillation (b. p. 155—156°/22 mm.) and subsequent crystallisation from toluene. The yield was 20 g. (53%), and the m. p. 64—65°.

Treatment of the *trans*-diol in pyridine with the appropriate acid chloride (2·2 mols.) for 2 days at 0°, followed by removal of most of the pyridine under reduced pressure below 40° and dilution of the residue with crushed ice, gave : the *bis*-3 : 5-*dinitrobenzoate*, plates (from benzene), m. p. 164—165° (after being dried in high vacuum at 100°) (Found : C, 48·5; H, 3·7; N, 10·7. $C_{21}H_{18}O_{12}N_4$ requires C, 48·65; H, 3·5; N, 10·8%); the *ditoluene*-p-*sulphonate*, needles (from methanol), m. p. 112° (Found : C, 57·8; H, 6·2; S, 14·3. $C_{21}H_{26}O_6S_2$ requires C, 57·5; H, 6·0; S, 14·6%); and the *dimethanesulphonate*, plates (from methanol), m. p. 104° (Found : C, 37·9; H, 6·1; S, 22·3. $C_{19}H_{18}O_6S_2$ requires C, 37·8; H, 6·3; S, 22·4%).

cis-cyclo*Heptane*-1 : 2-*diol*.—A solution of potassium permanganate (12·8 g.) and magnesium sulphate heptahydrate (20 g.) in water (600 c.c.) was added during 5 hr. to a vigorously stirred solution of *cyclo*heptene (9·6 g.) in ethanol (250 c.c.) kept at *ca.* −40°. The cooling bath was then removed, and the mixture kept overnight at room temperature. The solid was filtered off and washed with water, and the filtrate and washings were concentrated to small bulk and continuously extracted with ether, to give the *cis*-diol (4·5 g., 35%), m. p. 46—47° after recrystallisation from dry ether.

The following derivatives were prepared as described for the *trans*-isomers : the cis-*bis*-3 : 5-*dinitrobenzoate*, yellow needles (from chloroform–ethanol–dioxan), m. p. 96° (Found : C, 49·3; H, 4·1%); the cis-*ditoluene*-p-*sulphonate*, plates (from benzene–light petroleum), m. p. 104—105° (Found : C, 57·8; H, 6·2; S, 14·8%); and the cis-*dimethanesulphonate*, plates (from ether), m. p. 50° (Found : C, 37·75; H, 6·4; S, 22·4%).

cyclo*Heptene Oxide*.—Reaction of *cyclo*heptene (9·6 g.) with perbenzoic acid (21·9 g.) in dry chloroform (300 c.c.) (*Org. Synth.*, Coll. Vol. I, 2nd ed., p. 431; cf. Traube, *Chem. Eng. News*, 1949, **27**, 46) was complete in 48 hr. at 0°, as judged from occasional estimations of per-acid content in the mixture. The solution was then freed from acid by washing it with aqueous sodium carbonate, and was dried ($Na_2SO_4$) and evaporated to an oil, distillation of which furnished *cyclo*heptene oxide (8·9 g.), b. p. 65—67°/25 mm., $n_D^{22}$ 1·4620. Derx (*loc. cit.*) gave b. p. 161°, $n_D^{18\cdot5}$ 1·46499, but recorded no yield.

*Reactions of* cyclo*Heptene Oxide with Hydrogen Halides*.—(i) *With hydrogen chloride*. 0·9N-Ethereal hydrogen chloride (15 c.c.) was slowly added to a solution of *cyclo*heptene oxide (1·1 g.) in dry ether (10 c.c.) at 0°. After 6 hr. at room temperature, the solution was washed with water and with aqueous sodium hydrogen carbonate, then dried ($Na_2SO_4$) and evaporated, to give *trans*-2-chloro*cyclo*heptanol (0·7 g.), b. p. 45°/0·5 mm., $n_D^{21}$ 1·4960. When a portion was heated with 10% aqueous sodium hydroxide it gave *cyclo*heptene oxide (characteristic

odour). Another portion, with 3 : 5-dinitrobenzoyl chloride in pyridine, gave trans-2-*chloro*cyclo*heptyl* 3 : 5-*dinitrobenzoate*, which crystallised from chloroform–methanol in needles, m. p. 113° (Found : C, 48·9; H, 4·4; N, 8·0. $C_{14}H_{15}O_6N_2Cl$ requires C, 49·05; H, 4·4; N, 8·2%).

(ii) *With hydrogen bromide.* Dry hydrogen bromide was passed into a solution of *cyclo*heptene oxide (1·1 g.) in dry ether (15 c.c.) at 0° until no more was absorbed. The solution was then worked up as above to yield a liquid (1·3 g.), b. p. 53°/0·01 mm., $n_D^{18}$ 1·5310, consisting of *trans*-bromohydrin, probably containing some 1 : 2-dibromo*cyclo*heptane (Found : C, 40·5; H, 6·1. Calc. for $C_7H_{13}OBr$ : C, 43·5; H, 6·7%). It readily furnished trans-2-*bromo*cyclo*heptyl* 3 : 5-*dinitrobenzoate*, flattened needles (from chloroform–ethanol), m. p. 121° (Found : C, 43·4; H, 4·1; N, 6·9. $C_{14}H_{15}O_6N_2Br$ requires C, 43·4; H, 3·9; N, 7·2%).

(iii) *With hydrogen iodide.* Similar reaction of the oxide (1·1 g.) in dry ether (15 c.c.) with dry hydrogen iodide gave trans-2-iodo*cyclo*heptanol, $n_D^{19}$ 1·5630, which decomposed on attempted distillation. The crude product gave the 3 : 5-*dinitrobenzoate*, needles (from methanol), m. p. 134° (Found : N, 6·4. $C_{14}H_{15}O_6N_2I$ requires N, 6·45%).

*Monoacetate of* trans-cyclo*Heptane*-1 : 2-*diol*.—A solution of *cyclo*heptene oxide (1·1 g.) in acetic acid (5 c.c.) was kept at 100° for 15 hr. and then distilled, to give the trans-*monoacetate* (1·0 g.), b. p. 81—82°/0·5 mm., $n_D^{17}$ 1·4670 (Found : C, 62·8; H, 9·3. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%).

With 3 : 5-dinitrobenzoyl chloride in pyridine it gave the trans-*acetate* 3 : 5-*dinitrobenzoate*, which crystallised from benzene in plates, m. p. 96—97° (Found : C, 52·7; H, 5·1; N, 7·9. $C_{16}H_{18}O_8N_2$ requires C, 52·45; H, 4·95; N, 7·65%).

*Monotoluene*-p-*sulphonate of* trans-cyclo*Heptane*-1 : 2-*diol*.—A solution of *cyclo*heptene oxide (15 g.) in dry ether (50 c.c.) was added during 40 min. to a cooled and stirred suspension of toluene-*p*-sulphonic acid (27·5 g.) in dry ether (70 c.c.), the temperature being kept at *ca.* 0°. The resulting clear solution was kept at room temperature overnight, then washed with ice-water (2 × 30 c.c.), dried ($Na_2SO_4$), and evaporated below 30°, the last traces of solvent being removed at $10^{-4}$ mm.; the trans-*monotoluene*-p-*sulphonate* was a viscous oil (23·6 g.), $n_D^{18}$ 1·5300, which could not be distilled without decomposition (Found : S, 10·8. $C_{14}H_{20}O_4S$ requires S, 11·3%). When warmed with aqueous sodium hydroxide it gave *cyclo*heptene oxide (characteristic odour; no precipitate with 2 : 4-dinitrophenylhydrazine sulphate).

Treatment of the monotoluene-*p*-sulphonate with the appropriate acid chloride in pyridine for 24 hr. at 0° gave the following derivatives : the *trans*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 112°; the trans-*methanesulphonate toluene*-p-*sulphonate*, needles (from methanol), m. p. 120° (Found : C, 49·8; H, 6·2; S, 18·0. $C_{15}H_{22}O_6S_2$ requires C, 49·7; H, 6·1; S, 17·7%); and the trans-*benzoate toluene*-p-*sulphonate*, needles (from methanol), m. p. 101° (Found : C, 64·9; H, 6·3; S, 8·2. $C_{21}H_{24}O_5S$ requires C, 64·9; H, 6·2; S, 8·25%).

*Monomethanesulphonate of* trans-cyclo*Heptane*-1 : 2-*diol*.—Interaction of *cyclo*heptene oxide (2·2 g.) in dry ether (10 c.c.) with methanesulphonic acid (2·3 g.) in dry ether (15 c.c.) was carried out as for the reaction with toluene-*p*-sulphonic acid (see above), and gave the crude *trans*-monomethanesulphonate as an oil (2·4 g.), $n_D^{18}$ 1·4870 (Found : S, 13·8. Calc. for $C_8H_{16}O_4S$ : S, 15·4%). With the appropriate acid chloride in pyridine it gave : the *trans*-dimethanesulphonate, m. p. and mixed m. p. 104°; the *trans*-methanesulphonate toluene-*p*-sulphonate, m. p. and mixed m. p. 120°; and the trans-*methanesulphonate* 3 : 5-*dinitrobenzoate*, needles, m. p. 106° (from methanol) (Found : C, 45·1; H, 4·7; N, 6·7. $C_{15}H_{18}O_9N_2S$ requires C, 44·8; H, 4·5; N, 7·0%).

*Acetate Toluene*-p-*sulphonate of* trans-cyclo*Heptane*-1 : 2-*diol*.—Acetic anhydride (10·5 g.) in pyridine (20 c.c.) was added to a stirred solution of the *trans*-monotoluene-*p*-sulphonate (21 g.) in pyridine (50 c.c.) at 0°. The mixture was kept for 24 hr. at room temperature and then diluted with water and worked up by chloroform-extraction in the usual way. Evaporation of the washed and dried extracts gave the trans-*acetate toluene*-p-*sulphonate* as an oil (20 g.), $n_D^{18}$ 1·5130 (Found : S, 9·8. $C_{16}H_{22}O_5S$ requires S, 9·8%).

*Monoacetate of* cis-cyclo*Heptane*-1 : 2-*diol*.—(i) The *trans*-acetate toluene-*p*-sulphonate (2·6 g.), ethanol (40 c.c.), and calcium carbonate (3·4 g.) were boiled together under reflux for 46 hr. The mixture was then cooled, filtered, concentrated to small bulk, and diluted with water; the precipitated oil was isolated by extraction with ether, and on distillation furnished a main fraction (0·7 g.), b. p. 87—89°/0·5 mm., $n_D^{19}$ 1·4720, which was probably a mixture of the acetate and the ethyl ether (Found: C, 64·6; H, 9·6; OEt, 3·0. Calc. for $C_9H_{16}O_3$ : C, 62·8; H, 9·3. Calc. for $C_{11}H_{20}O_3$ : C, 66·0; H, 10·1; OEt, 22·5%).

(ii) A mixture of *trans*-acetate toluene-*p*-sulphonate (7·6 g.), calcium carbonate (7·5 g.), acetone (55 c.c.), and water (55 c.c.) was boiled under reflux for 2 days, and was then filtered

and worked up as above, to give the cis-*monoacetate* (1·8 g.), b. p. 89—90°/0·5 mm., $n_D^{21}$ 1·4718 (Found: C, 63·0; H, 9·5. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%). With 3 : 5-dinitrobenzoyl chloride in pyridine it gave the cis-*acetate* 3 : 5-*dinitrobenzoate*, leaflets (from methanol), m. p. 53° (Found: C, 52·5; H, 4·9. $C_{16}H_{18}O_8N_2$ requires C, 52·45; H, 4·95%).

Treatment of the *cis*-monoacetate (0·44 g.) with sodium (0·05 g.) in dry methanol (20 c.c.) for 24 hr. at room temperature, followed by neutralisation with carbon dioxide, evaporation to dryness, and extraction of the residue with dry ether, furnished, on evaporation of the extracts, the *cis*-diol (0·26 g.), m. p. 44—46°, characterised as the *cis*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 103°.

*Acetate Toluene*-p-*sulphonate of* cis-cyclo*Heptane*-1 : 2-*diol*.—Reaction of the *cis*-monoacetate (5·7 g.) with toluene-*p*-sulphonyl chloride (9·5 g.) in pyridine (25 c.c.) at 0° gave the cis-*acetate toluene*-p-*sulphonate* as an oil (9·0 g.), $n_D^{22}$ 1·5110 (Found: S, 9·8. $C_{16}H_{22}O_5S$ requires S, 9·8%).

*Monotoluene*-p-*sulphonate of* cis-cyclo*Heptane*-1 : 2-*diol*.—A solution of toluene-*p*-sulphonyl chloride (3·4 g.) in pure chloroform (30 c.c.) was added in small portions during 3 days to a solution of the *cis*-diol (2·35 g.) in pyridine (20 c.c.) at 0°. The mixture was kept at 0° for two more days and was then diluted with chloroform (75 c.c.) and washed successively with 2N-sulphuric acid, aqueous sodium hydrogen carbonate, and water. Evaporation of the dried ($Na_2SO_4$) chloroform solution at 30° under reduced pressure, finally at $10^{-3}$ mm., gave the cis-*monotoluene*-p-*sulphonate* as a viscous oil (3·1 g.), $n_D^{23}$ 1·5312 (Found: S, 10·7. $C_{14}H_{20}O_4S$ requires S, 11·3%).

Treatment of a small portion of the product with toluene-*p*-sulphonyl chloride in pyridine gave the *cis*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 103°. Reaction of another portion with benzoyl chloride in pyridine gave the cis-*benzoate toluene*-p-*sulphonate*, which crystallised from methanol in needles, m. p. 86° (Found: C, 64·6; H, 6·4; S, 8·6. $C_{21}H_{24}O_5S$ requires C, 64·9; H, 6·2; S, 8·25%).

*Reactions of the Monotoluene*-p-*sulphonates with Metallic Salts*.—(a) *Lithium chloride*. (i) A solution of the *trans*-monotoluene-*p*-sulphonate (2 g.) and lithium chloride (1·4 g.) in ethanol (25 c.c.) was boiled under reflux for 24 hr. and then concentrated to small volume and diluted with water (25 c.c.). The precipitated oil, isolated by extraction with ether, on distillation gave *trans*-2-chloro*cyclo*heptanol (0·4 g.), b. p. 48—50°/0·6 mm., $n_D^{14}$ 1·4938, characterised as the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 113°.

(ii) Similar treatment of the *cis*-monotoluene-*p*-sulphonate (0·8 g.) with lithium chloride (1·0 g.) in ethanol (10 c.c.) also gave the *trans*-chlorohydrin (0·2 g.), b. p. 100°/15 mm., $n_D^{20}$ 1·4865 (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 112°). The crude chlorohydrin gave a slight precipitate with 2 : 4-dinitrophenylhydrazine sulphate, and probably contained a small amount of *cyclo*heptanone.

(b) *Lithium bromide*. The *trans*-monotoluene-*p*-sulphonate (2·5 g.) and lithium bromide (2·9 g.) in acetone (20 c.c.) were boiled under reflux for 4 hr.; lithium toluene-*p*-sulphonate (0·73 g.), which had been gradually deposited, was then filtered off. The filtrate did not give any more solid on further heating, and it was concentrated and worked up with water and ether as described above, to yield *trans*-2-bromo*cyclo*heptanol (1·2 g.), b. p. 55—56°/0·4 mm., $n_D^{20}$ 1·5175, identified as the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 121°.

(ii) The *cis*-acetate toluene-*p*-sulphonate (3·0 g.), on similar treatment for 5 hr. with lithium bromide (2·0 g.) in acetone (15 c.c.), gave, on evaporation of the ethereal extracts, a crude acetate bromide, which was dissolved in 0·2N-methanolic hydrogen chloride (25 c.c.) and kept for 16 hr. at room temperature. Evaporation of this solution and distillation of the residual oil gave a main fraction (0·6 g.), b. p. 70—72°/1 mm., $n_D^{22}$ 1·5008, which furnished the same *trans*-3 : 5-dinitrobenzoate, m. p. and mixed m. p. 121°.

(c) *Sodium iodide*. When a solution of the *trans*-monotoluene-*p*-sulphonate (2·1 g.) and sodium iodide (3·6 g.) in acetone (20 c.c.) was boiled under reflux for 20 min., it became brown and deposited sodium toluene-*p*-sulphonate (1·2 g.). The filtrate was worked up as described above (except that the ethereal extract was washed with aqueous sodium thiosulphate) and furnished crude *trans*-2-iodo*cyclo*heptanol (1·2 g.), $n_D^{20}$ 1·5685, identified as the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 134°.

*Formation of* cyclo*Heptanone from the* cis-*Monotoluene*-p-*sulphonate*.—(i) The monotoluene-*p*-sulphonate (0·57 g.) in 0·1N-methanolic potassium hydroxide (40 c.c.) was set aside for 5 days at room temperature. Back-titration with standard acid showed that the reaction was then complete, and the solution was acidified and treated with excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate. The precipitated derivative was collected, washed with water, and dried

(yield, 0·46 g., 80%); one recrystallisation from ethanol gave *cyclo*heptanone 2 : 4-dinitrophenylhydrazone, m. p. 145°.

(ii) A solution of the *cis*-acetate toluene-*p*-sulphonate (2·5 g.) in ethanol (10 c.c.) and 2N-aqueous sodium hydroxide (20 c.c.) was boiled under reflux for 1 hr. and then steam-distilled. The distillate gave *cyclo*heptanone 2 : 4-dinitrophenylhydrazone (1·5 g., 67%), m. p. 144°.

*Rates of Reaction of the Monotoluene*-p-*sulphonates with Alkali.*—(i) *trans-cyclo*Heptane-1 : 2-diol monotoluene-*p*-sulphonate (0·568 g.) was diluted with methanol to 40 c.c., and the temperature adjusted to 20°. A 5-c.c. portion was diluted with methanol (40 c.c.) at 20°, then rapidly mixed with 5 c.c. of 0·0875N-methanolic potassium hydroxide, also at 20°, thus giving a 0·005M-solution of the ester in 0·00875N-alkali, and kept at this temperature for a known time before being titrated directly with 0·107N-sulphuric acid (phenolphthalein indicator). Preliminary experiments indicated the approximate titres for various times of reaction, and in the final experiments about 90% of the required amount of acid was added in one lot, and the titration completed within about 10 sec. In spite of the rapidity of the reaction, results obtained in this way were indistinguishable from those found by stopping of the reaction by addition of excess of acid, followed by back-titration with standard alkali.

The % reaction was: 33 (2 min.); 57 (5 min.); 78 (10 min.); 95 (30 min.). The corresponding values of $k_2$ were 25, 24, 25, and 20 mole l.$^{-1}$ min.$^{-1}$.

(ii) *cis-cyclo*Heptane-1 : 2-diol monotoluene-*p*-sulphonate (0·421 g.) was dissolved in 0·086N-methanolic potassium hydroxide (40 c.c.) at 20° (to give a 0·037M-solution of ester) and kept at that temperature. The % reaction, determined as described above, was: 9 (1 hr.); 23 (3½ hr.); 58 (21 hr.); 81 (45 hr.); the corresponding values of $k_2$ were 0·017, 0·014, 0·009, and 0·009 mole l.$^{-1}$ min.$^{-1}$.

(iii) *trans-cyclo*Hexane-1 : 2-diol monotoluene-*p*-sulphonate (Criegee and Stanger, *Ber.*, 1936, **69**, 2753) (0·540 g.) was diluted with methanol to 40 c.c.; experiments were carried out as described above, on 5-c.c. portions mixed at 20° with 5 c.c. of 0·090N-methanolic potassium hydroxide. The % reaction was: 70 (2½ min.); 89 (5 min.); 95 (10 min.); and the corresponding values of $k_2$ were 14·2, 15·1, and 11·0 mole l.$^{-1}$ min.$^{-1}$.

Microanalyses were carried out in the Microanalytical Laboratory of this Department (Mr. F. H. Oliver). One of us (G. S. S.) is grateful to the University of Delhi for the grant of one year's study-leave.

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## 527. *Studies on the Behaviour of Halides of the Transition Metals with Ammonia. Part II.* The Reaction of Titanium Tetrachloride with Ammonia.*

By G. W. A. Fowles and F. H. Pollard.

The reaction between titanium tetrachloride and ammonia has been investigated tensimetrically at temperatures between −36° and −63°, and explained by the formation of amidochlorides, *e.g.*, $Ti(NH_2)_3Cl$. Thermal decomposition of the products in vacuum at 350° gave TiNCl.

An improved apparatus is described for the study of reactions in liquid ammonia.

The reaction of titanium tetrachloride with ammonia was first studied by Rose (*Pogg. Ann.*, 1829, **16**, 57) and Persoz (*Ann. Chim. Phys.*, 1830, [ii], **44**, 321) who reported the formation of yellow compounds, $TiCl_4,4NH_3$ and $TiCl_4,6NH_3$, respectively. When the latter compound was left in a desiccator over calcium chloride, it became colourless with the loss of two molecules of ammonia, and, after extraction of this material with liquid ammonia, another colourless substance was obtained which was thought to be the amide, $Ti(NH_2)_4$ (Rosenheim and Schutte, *Z. anorg. Chem.*, 1901, **26**, 245; Blix, *Ber.*, 1903, **36**, 4228). Stahler (*Ber.*, 1905, **38**, 2619), however, observed that the initial hexammoniate

* Part I, *J.*, 1952, 4938.

was hydrolysed under the conditions used by the former workers, yielding a mixture of titanium hydroxide and ammonium chloride with a similar overall titanium content. He also reported a complex, $TiCl_4,8NH_3$, which on extraction with liquid ammonia gave a dark yellow amide, $Ti(NH_2)_4$.

The work of Blix and of Stahler was repeated by Ruff and Eisner (*Ber.*, 1908, **41**, 2250), who were unable to obtain a completely chlorine-free substance even on prolonged washing with liquid ammonia. When the washed product was thermally decomposed at 300° in vacuum, a blue-black substance was formed, which Ruff claimed to be impure titanium nitrogen chloride, TiNCl, but his analytical results suggest that the product was contaminated with an appreciable amount of hydrolysed material. This would be expected, since the washed product was transferred to a porcelain boat for the decomposition, without any precautions to exclude moisture.

More recently, Brager (*Acta Physicochim. U.R.S.S.*, 1939, **10**, 887) has made a thorough *X*-ray study of the thermal decomposition of the $TiCl_4,4NH_3$ complex (which is formed at room temperature). He found that, at 200°, the complex changed from its initial deep yellow to a greyish-green colour, without alteration in composition. A greenish-brown substance, having a variable composition, was formed at 300°, changing to TiNCl at 350°. Prolonged heating above 400° gave the nitride, TiN, and chlorine.

Since the nature of the complexes which are formed initially has not been previously investigated, we have (*a*) produced materials of maximum ammonolysis, and (*b*) investigated the $TiCl_4$–$NH_3$ system tensimetrically. (*a*) The products would be expected to show the greatest ammonolysis at high reaction temperatures, and after prolonged washing with liquid ammonia to remove any ammonium chloride which was formed. (Ammonium chloride is very soluble, and the titanium complex insoluble, in liquid ammonia.) The reaction has therefore been carried out at the boiling point of liquid ammonia (−33·5°) and at room temperature (in a Carius tube), and the product extracted with liquid ammonia. (*b*) Our tensimetric studies were made at reaction temperatures of −36° and −63°, followed by the thermal decomposition of the product *in vacuo* to a temperature of 350°.

## Experimental

Titanium tetrachloride was obtained in ampoules from British Drug Houses and condensed under vacuum into thin-walled bulbs (Found : Ti, 25·20; Cl, 74·7. Calc. for $TiCl_4$ : Ti, 25·25; Cl, 74·75%). Ammonia was purified as described in Part I (*loc. cit.*).

*Reaction between Ammonia and Titanium Tetrachloride.*—The reaction at −63° and −36° has been followed by a method similar to that described for the niobium pentachloride–ammonia reaction (Part I, *loc. cit.*). The resulting pressure–composition values are plotted in Fig. 1, curves (*a*) and (*b*) respectively. Both curves are perfectly reproducible in their general shape. After the removal of excess of ammonia at the reaction temperature, the complex remaining had an overall composition corresponding to $TiCl_4,8NH_3$.

*Thermal Decomposition of* $TiCl_4,8NH_3$.—This complex appeared to be the same no matter what the original reaction temperature was, being a very pale yellow, easily hydrolysed substance, which decomposed liberating ammonia when heated over the temperature range −30° to 300°. In order to investigate the possibility of stable intermediate complexes, the initial compound was heated for 2 hr. at 20°-intervals up to 220°, any gases liberated being trapped in a bulb cooled in liquid oxygen, and their nature (ammonia in every case) and amount determined. A typical variation of composition with temperature is shown in Fig. 2.

The colour of the complex deepens as ammonia is removed, becoming orange-yellow when the composition $TiCl_4,2NH_3$ is reached at 180°. On further heating, the product changed to a brick-red, apparently homogeneous substance at 240°, and to a dark green material at 300°. During these heatings, a sublimate appeared on the cooler part of the stem of the reaction bulb, varying in colour from deep red near the hot bulb to yellow in the coolest part. These colours remained if the bulb was allowed to cool to room temperature. No gas pressure was recorded on the manometer during these decompositions, although traces of titanium tetrachloride were found in the tap grease, and could be condensed over into the calibrated bulb.

While the red compound formed at 240° was hydrolysed quite easily, the greenish-black substance was hydrolysed only slowly in water but decomposed readily in concentrated nitric

acid. The red compound is evidently a mixture, its analysis (Ti, 39·85; N, 15·2; Cl, 44·2%) corresponding to the ratio $Ti_1N_{1\cdot33}Cl_{1\cdot50}$. The greenish-black material gave analyses corresponding to ratios varying from $Ti_1N_{1\cdot34}Cl_{1\cdot41}$ (after 2 hr.' heating at 300°) to $Ti_1N_{0\cdot97}Cl_{1\cdot04}$ (after 2 hr.' heating at 350°), the total percentage in every analysis being between 99 and 100.

Samples of all these compounds were found to be slightly diamagnetic, thus precluding the possibility of any lower valency state for titanium.

*Reaction of Ammonia with Titanium Tetrachloride at −33·5° (b. p. of ammonia), followed by Washing with Liquid Ammonia.*—Several workers have devised an apparatus with which it is possible to achieve some measure of filtration with solutions in liquid ammonia, among whom may be mentioned Schwarz and Schenk (*Ber.*, 1930, **63**, 296) and Thomas and Pugh (*J.*, 1931, 60): both were concerned with the ammonolysis of germanium compounds. The simple apparatus of Thomas and Pugh needed rebuilding after each experiment, and decomposition studies were not possible. Schwarz and Schenk, on the other hand, designed an intricate system in which many operations would become extremely tedious, if not impossible: a severely modified and simplified version of this apparatus was used in our experiment, the final form being shown in Fig. 3. Reaction vessel *D* contained a sintered glass filter *M* of porosity 3. The ammonia was stored in *B* and could be transferred to any other part of the apparatus

FIG. 1.

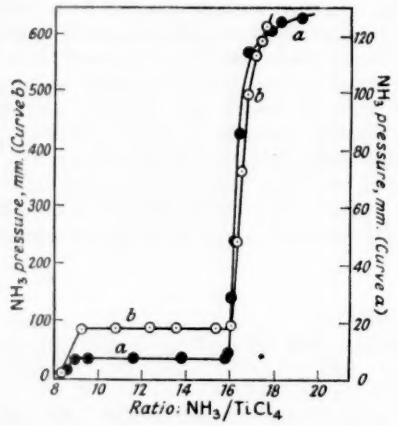
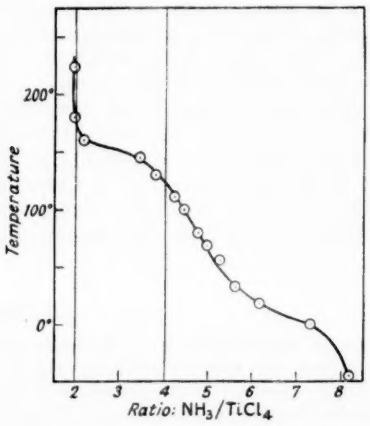



FIG. 2.




by condensation, while *E* was a jointed bulb containing sodium to be used for purifying the ammonia, which was then used again and again for washing. Safety valves, *H*, *I*, *J*, and *K*, in the form of manometer bubblers, were provided in those parts of the apparatus where excessive pressures of ammonia might develop.

*Method of using the Apparatus.*—Liquid ammonia from the cylinder was placed in trap *A*, and sodium added until a permanent blue colour was observed. The ammonia was allowed to evaporate through bubbler *H*, until all the air in the apparatus had been displaced, final traces being removed by surrounding *A* with a cold bath (−35° to −40°), closing tap 1, and evacuating the storage vessel with the pump. The ammonia was then condensed into *B* by means of a solid carbon dioxide bath. Freezing out with liquid oxygen was avoided, since *A* cracked on a number of occasions.

*n*-Pentane, which had been carefully dried ($MgSO_4$), was condensed into *C*. A sealed bulb of titanium tetrachloride was placed in a jointed tube, together with a glass-encased ball bearing, and, when air had been removed by the pump, was broken magnetically. The titanium chloride was then condensed on to the pentane in *C*, and a clear solution obtained by warming to room temperature. Ammonia was condensed into *D* from *B* until the filter *M* was covered, and then the pentane solution was run over from *C* into *D* by opening tap 2 (the vapour pressure of the pentane solution being sufficient to push the solution over). A further layer of ammonia was condensed on the titanium tetrachloride solution layer, and the whole allowed to warm to −33·5°. After 2 hr., the ammonia and pentane were pumped away, and a further quantity of ammonia was condensed in the reaction vessel and allowed to boil gently. The solution was

agitated magnetically—a glass-encased steel ball being previously placed on the filter. The liquid ammonia was filtered over into *E* (evacuated and surrounded by a solid carbon dioxide bath) by opening tap 3, undue evaporation of the ammonia being prevented by surrounding the tubing from *D* to *E* with asbestos string. The purified ammonia was then condensed back into the storage vessel *B* by way of the glass-wool filter *G* and tap 4. Further quantities of ammonia were condensed on to the reaction products and again filtered off, the process being repeated until the washings were free from ammonium chloride, as shown when no further hydrogen was liberated in *E* ($NH_4Cl + Na = NaCl + NH_3 + \frac{1}{2}H_2$). The product was then allowed to warm to room temperature, and pumped hard with the high-vacuum pump for 1 hr. to remove any absorbed ammonia. A stream of nitrogen (purified in the usual way over $P_2O_5$ and heated Cu) was flushed through the filter, escaping by way of bubbler *J*, and the reaction vessel was removed and the product shaken into a weighed jointed tube for analysis.

Samples of the deep yellow product remaining after twelve washes were analysed (see Table 1), the total percentage in every case being between 96 and 97. The ratios varied between $Ti_1N_{3\cdot42}Cl_{1\cdot20}$ and $Ti_1N_{3\cdot11}Cl_{1\cdot03}$, the majority of the analyses approaching the second ratio. Since the precautions taken eliminate the possibility of hydrolysis of the product with

FIG. 3.

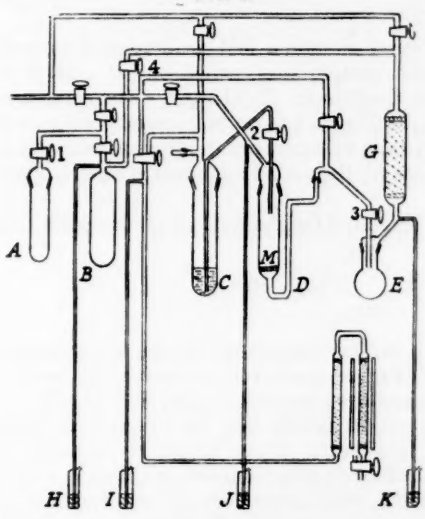
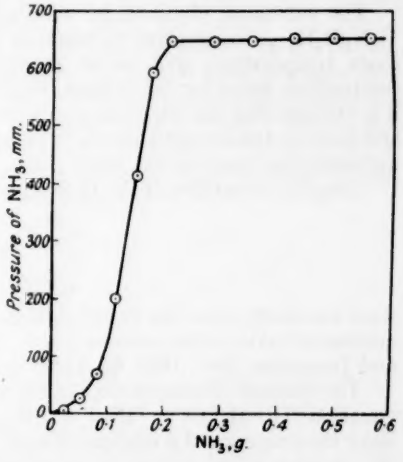



FIG. 4.




consequent oxide contamination, the persistent 3—4% deficiency in the total analysis may be assumed to be hydrogen, giving the substance an empirical formula $Ti_1N_3Cl_1H_{4-6}$.

*Reaction in Sealed Carius Tubes, followed by Washing with Liquid Ammonia.*—Even extensive washing of the low-temperature reaction product failed to replace the last chlorine atom, so in an attempt to achieve complete ammonolysis, titanium tetrachloride and ammonia were condensed into a Carius tube, sealed off, and allowed to react at room temperature. After 5 days, the tube was cooled to −33°, and its tip scored and hot-spotted. A length of Polythene tubing was quickly slipped over the Carius tube, whose contents were then poured rapidly into

TABLE 1. *Typical analyses for the washed product from the* $TiCl_4$–$NH_3$ *reaction.*

| No. | Ti, % | N, % | Cl, % | Total, % | Ratio Ti : N : Cl |
|---|---|---|---|---|---|
| 1 | 33·4 | 33·4 | 29·7 | 96·5 | 1 : 3·42 : 1·20 |
| 2 | 34·3 | 33·9 | 28·9 | 97·1 | 1 : 3·38 : 1·12 |
| 3 | 35·9 | 32·7 | 27·4 | 96·0 | 1 : 3·11 : 1·03 |
| 4 | 35·0 | 33·1 | 28·3 | 96·4 | 1 : 3·23 : 1·09 |

the filter vessel. Hydrolysis during this transference was reduced to a minimum by passing a steady stream of dried nitrogen through the filter vessel. After excess of ammonia had evaporated away, the pale yellow product was pumped hard and washed with liquid ammonia in the usual way. The deep yellow material produced in this way appeared to be identical

with the low-temperature washed product in both appearance and composition (Table 2), and in no experiment did the Ti : Cl ratio exceed 1 : 1.

TABLE 2. *Typical analyses for the washed product (Carius tube).*

| No. | Ti, % | N, % | Cl, % | Total, % | Ratio Ti : N : Cl |
|---|---|---|---|---|---|
| 1 | 34·0 | 31·4 | 29·7 | 95·1 | 1 : 3·16 : 1·18 |
| 2 | 34·0 | 32·7 | 29·0 | 95·7 | 1 : 3·28 : 1·15 |

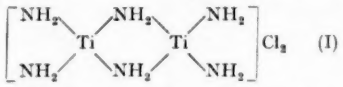
*Tensimetric Study of the Washed Product.*—A weighed sample (0·303 g.) was placed in the reaction bulb, a known excess of ammonia condensed on it, and a tensimetric curve (Fig. 4) obtained in the usual way.

*Thermal Decomposition of the Washed Product.*—When heated *in vacuo*, the product liberated almost 2 mol. of ammonia between 100° and 220°, becoming very deep red-brown. When heated to 380° for 2 hr., the product became black, and liberated a small amount of ammonia—making 2 mol. in all. Only a very small amount of yellow sublimate formed on the cooler part of the tube. Analysis of the black sample gave the following figures: Ti, 47·8; N, 14·6; Cl, 35·9%, corresponding to Ti : N : Cl = 1 : 1·04 : 1·01.

## DISCUSSION

The substance obtained by washing with liquid ammonia had an empirical formula $Ti_1N_3Cl_1H_{4-6}$, irrespective of whether the initial reaction was carried out at −33·5° or room temperature, and is no doubt the amidochloride $Ti(NH_2)_3Cl$. The pressure–composition curve for the system $NH_3$–$Ti(NH_2)_3Cl$ (Fig. 4) has no univariant portion, and it is evident that the titanium complex does not take up ammonia to form an ammoniate, and that no ammonium chloride is present. Since all the added ammonia is exactly given up, no further reaction has taken place.

Complex structures of the type (I) could be suggested for the washed product, but they



(I)

seem less likely since the tetrachlorides of silicon and germanium are known to give simple amides or imides when ammonolysed. Stannic chloride, moreover, is reported by Schwarz and Jeanmaire (*Ber.*, **1932**, **65**, 1443) to give the analogous amidochloride, $Sn(NH_2)_3Cl$.

The thermal decomposition of the titanium amidochloride may be represented by the equation $Ti(NH_2)_3Cl = TiNCl + 2NH_3$. Our tensimetric study might be expected to show the existence of a mixture of such an amidochloride with ammonium chloride, though the reaction might not go to completion until the ammonium chloride was removed by washing with ammonia. The pressure–composition curves (Fig. 1) show three sections, as with those obtained for the ammonium chloride–ammonia reaction (Part I, *loc. cit.*), and it is evident that 16 molecules of ammonia initially react with one of titanium tetrachloride, $TiCl_4 + 16NH_3 = TiCl_4,16NH_3$, 8 being removed by a univariant process leaving $TiCl_4,8NH_3$. The pressure of this univariant step corresponds to the dissociation of ammonium chloride triammoniate, suggesting the formation of $2\frac{2}{3}$ moles of ammonium chloride, *i.e.*, the initial reaction is represented by the stoicheiometric equation:

$$3TiCl_4 + 48NH_3 = 2Ti(NH_2)_3Cl + Ti(NH_2)_2Cl_2,8NH_3 + 8NH_4Cl,3NH_3$$

so that the product contains two amidochlorides. The ammonium chloride loses its ammonia in a vacuum at the reaction temperature, leaving a mixture of ammonium chloride and amidochlorides, with the overall composition $TiCl_4,8NH_3$ [*i.e.*, $2Ti(NH_2)_3Cl + Ti(NH_2)_2Cl_2,8NH_3 + 8NH_4Cl$]. When this mixture is heated to 180° *in vacuo*, its composition changes to $TiCl_4,2NH_3$ (*i.e.*, without loss of hydrogen chloride), so it is not possible to account for the presence of $2\frac{2}{3}$ moles of ammonium chloride at this stage.

The two possibilities are: (1) The ammonium chloride present reacts with the product on heating, liberating ammonia. (2) The length of the univariant portion of the tensimetric curve is not proportional to the amount of ammonium chloride present. The

first possibility is perhaps the more likely. The ammonium chloride initially formed will be taken into solution by the excess of ammonia present, and an equilibrium position reached. It is not possible to prove the existence of this equilibrium tensimetrically, since the amount of ammonia needed to produce a measurable shift would be considerable, and the experimental error involved would be of similar significance. When excess of ammonia is removed, an intimate mixture of ammonium chloride and the amidochlorides exists, which might react on heating according to the equations:

(i) $Ti(NH_2)_3Cl + NH_4Cl = Ti(NH_2)_2Cl_2 + 2NH_3$

(ii) $Ti(NH_2)_2Cl_2 + NH_4Cl = Ti(NH_2)Cl_3 + 2NH_3$

(iii) $Ti(NH_2)Cl_3 + NH_4Cl = TiCl_4 + 2NH_3$

The thermal decomposition of the $TiCl_4,8NH_3$ complex is shown in Fig. 2, and since the general shape of this curve is reproducible under very varied conditions, the inflexion in the slope suggests the intermediate existence of $TiCl_4,4NH_3$. The ammonia held by amidochloride $Ti(NH_2)_2Cl_2$, by weak ion–dipole forces, would be easily lost, the amidochlorides then reacting with the ammonium chloride. Since $Ti(NH_2)_3Cl$ has been shown not to lose ammonia below 90°, it probably reacts with the ammonium chloride before it can split out ammonia, leaving the mixture $Ti(NH_2)_2Cl_2 + 2NH_4Cl$, with the overall composition $TiCl_4,4NH_3$. On continued heating, $Ti(NH_2)Cl_3$ is formed (see reaction ii), so the limiting composition obtained at 180° is the mixture $Ti(NH_2)Cl_3 + NH_4Cl$. When the temperature is raised still further, the amidochloride may react either with the ammonium chloride (see reaction iii), giving titanium chloride and ammonia (which react immediately outside the hot zone), or with other amidochloride molecules: $3Ti(NH_2)Cl_3 = 2TiCl_4 + 2NH_3 + TiNCl$, *i.e.*, (II). Both of these reactions are equally probable at high temperatures, and would no doubt take place simultaneously.

(II)

In such a complicated system, it is difficult, from phase-rule considerations, to see how a univariant step is obtained which is not a direct measure of the amount of ammonium chloride present, unless some mixed-crystal formation takes place, giving rise to equilibria of the type $Ti(NH_2)_nCl_{4-n},nNH_4Cl,yNH_3 = Ti(NH_2)_nCl_{4-n},nNH_4Cl + yNH_3$. Under these conditions, the complex could contain any quantity of ammonium chloride up to the maximum of $2\frac{2}{3}$ moles. Since $Ti(NH_2)_3Cl$ is formed on washing, it seems more likely that at least some of this will be present in the unwashed product.

A discussion of this reaction cannot be concluded without mentioning the chance of complex-ion formation. Anions of the type $[Ti(NH_2)_xCl_{6-x}]^{--}$ are not unlikely, and Schmitz-DuMont (*Angew. Chem.*, 1950, **62**, 560), for instance, has found titanium alkoxides to react with a solution of potassium in liquid ammonia, forming the salt $K_2[Ti(OR)_4(NH_2)_2]$. Such ions would, however, be expected to be soluble in liquid ammonia, whereas the titanium complex is a solid, insoluble in all the usual solvents, and so probably has a polymeric nature. Any amidochlorides present will, therefore, almost certainly not be monomeric.

TiNCl is produced on decomposition *in vacuo* at 350°, but in view of Brager's excellent *X*-ray study (*loc. cit.*), thermal decomposition of this substance was not studied in detail.

A discussion of the replacement of chlorine atoms by amido-groups, along the lines of Wardlaw's alcoholysis studies (*J.*, 1950, 3450), is reserved until a subsequent paper, when the study of the behaviour of the Group IVA metal tetrachlorides with ammonia will be completed.

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## 528. *Application of Molecular-orbital Theory to Some Binuclear Co-ordination Compounds.*

By J. D. Dunitz and L. E. Orgel.

Molecular-orbital theory is applied to some binuclear co-ordination compounds of transition metals. For the $(Ru_2Cl_{10}O)^{4-}$ ion the theory involves ruthenium–oxygen double bonding with consequent diamagnetism of the ion. The peroxo-cobalt decammines and iron enneacarbonyl are also discussed.

We have recently used molecular-orbital theory in discussing the structure and stability of di*cyclo*pentadienyliron (ferrocene) and related compounds (Dunitz and Orgel, *Nature*, **1953**, **171**, 121). Here, we apply the theory to some binuclear compounds containing transition metals, to show that, in certain cases, it provides a ready explanation of otherwise puzzling aspects of their molecular structure. We shall make considerable use of the theory of group representations and shall employ the nomenclature of Eyring, Walter, and Kimball ("Quantum Chemistry," Wiley, New York, 1944).

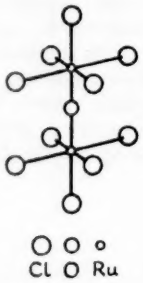



Fig. 1. *Atomic arrangement in* $(Ru_2Cl_{10}O)^{4-}$ *anion* (after Mathieson, Mellor, and Stephenson, *loc. cit.*).

*Potassium Hydroxychlororuthenate*, $K_4Ru_2Cl_{10}O,H_2O$.—Mathieson, Mellor, and Stephenson (*Acta Cryst.*, 1952, **5**, 185) have shown that potassium hydroxychlororuthenate contains an anion $(Ru_2Cl_{10}O)^{4-}$ with structure as in Fig. 1. Three features seem worthy of comment: (*a*) The substance is diamagnetic in spite of the fact that $Ru^{IV}$ would be expected to have two unpaired electrons. (*b*) The arrangement of Ru–O–Ru is linear. (*c*) The Ru–O bond distance is 1·80 Å, considerably shorter than the sum of single-bond radii, 1·98 Å. The Ru–Cl distance, however, is normal, 2·34 Å. The above authors suggest, as a possible explanation of the diamagnetism, that "the spins of the unpaired electrons on each $Ru^{IV}$ atom are antiparallel but uncoupled. Alternatively some type of electron pairing may take place." The nature of such electron pairing is not specified but a possible analogy with $Fe_2(CO)_9$ is suggested, whence it may be inferred that some type of interaction between the ruthenium atoms is postulated. In view of the long Ru · · · Ru distance, 3·6 Å, any strong direct action seems most unlikely. A footnote refers to a suggestion by Pauling that "if each ruthenium atom has seven orbitals of which two are required for bond formation with the oxygen atom, the diamagnetism would be explained," but Mathieson, Mellor, and Stephenson consider that the structure involving oxygen associated with two double bonds is improbable. We shall show that features (*a*), (*b*), and (*c*) all emerge from a qualitative molecular-orbital treatment which not only confirms Pauling's suggestion but also throws considerable light on the nature of the double bonding involved.

The symmetry of the complex anion is $D_{4h}$ but the local symmetry of each Ru atom is only $C_{4v}$. In the latter point group, the relevant orbitals transform as follows:

| | |
|---|---|
| $A_1$ | $s,p(z),d(z^2)$ |
| $B_1$ | $d(x^2-y^2)$ |
| $B_2$ | $d(xy)$ |
| $E$ | $d(xz,yz),p(x,y)$ |

giving a sum of representations $3A_1 + B_1 + B_2 + 2E$. The set of five σ-bonds formed by the chlorine atoms transform as $2A_1 + B_1 + E$ and the σ-bond to the oxygen atom trans-

forms as $A_1$, so that $B_2$ and $E$ are available for the four electrons of the $Ru^{IV}$ atom. These orbitals correspond to the triply degenerate $T_2$ orbitals of the octahedral paramagnetic $(Ru^{IV}Cl_6)^{2-}$ ion, and it is just this partial breakdown of the degeneracy in the lower symmetry group which removes the paramagnetism. Considering the two ruthenium atoms, now as a pair, these atomic orbitals combine to give new molecular orbitals, transforming (in the point-group $D_{4h} = C_{4v} \times i$) as $B_{2g}$, $B_{2u}$, $E_g$, and $E_u$. The filled degenerate $p(x,y)$ orbitals of the $O^{2-}$ ion transform as $E_u$. Clearly the two $E_u$ orbitals (one from the Ru pair and one from $O^{2-}$) combine to give a bonding $E_u{}^b$ and an antibonding $E_u{}^a$ orbital. The order of energy levels is therefore :

$$(E_u{}^b)[(B_{2g})(B_{2u})(E_g)](E_u{}^a)$$

where the orbitals in the square brackets are approximately degenerate. We now have to place 12 electrons [4 from each $Ru^{IV}$ together with the oxygen $p(x,y)$ set] and it is evident that the ground state is described by $(E_u{}^b)^4(B_{2g})^2(B_{2u})^2(E_g)^4(E_u{}^a)^0$ whence, since all electrons are in closed shells, the substance should be diamagnetic.

FIG. 2. *One of the two perpendicular components of the bonding $E_u{}^b$ π-orbital in $(Ru_2Cl_{10}O)^{4-}$ anion.*

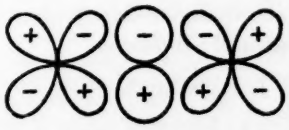
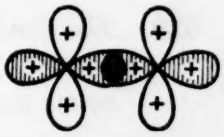


FIG. 3. *The $E_g{}^b$ (unshaded) and $A_{1g}$ (shaded) orbitals for $Fe_2(CO)_9$ projected on a plane.*



The $E_u{}^b$ orbital may be described as a degenerate bonding π-orbital (Fig. 2); the actual extent of π-bonding will be sensitive to the relative electronegativities of the atoms concerned, but the observed Ru–O distance, 1·80 Å, is close to the value 1·74 Å found in $RuO_4$ and indicates considerable double-bond character. It is clear too that the degree of π-bonding, and hence the stability of the anion, would be diminished by any departure from linearity of Ru–O–Ru. In valence-bond terms, the situation may perhaps be described as corresponding to resonance between a number of structures of which the extremes are $(Cl_5Ru^{IV}\text{–}\overset{2-}{O}\text{–}Ru^{IV}Cl_5)$ and $(Cl_5Ru^{II}{=}\overset{2+}{O}{=}Ru^{II}Cl_5)$.

*Peroxocobalt Decammines.*—The peroxocobalt decammines $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]X_4$ (I) are remarkable for the ease with which they may be oxidised to $[(NH_3)_5Co{\cdot}O_2{\cdot}Co(NH_3)_5]X_5$ (II), which have been regarded as the only compounds containing $Co^{IV}$ (see, *e.g.*, Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, p. 1420). The possibility that the oxidation involves removal of an electron from the oxygen rather than from the cobalt has, however, been suggested by several authors (Gleu and Rehm, *Z. anorg. Chem.*, 1938, **237**, 79; Malatesta, *Gazzetta*, 1942, **72**, 287; Thompson and Wilmarth, *J. Phys. Chem.*, 1952, **56**, 5). Our discussion of the previous section may be applied directly to the ion (I), provided it is linear, the only difference being that the oxygen has now both internally bonding $E_u(w\pi)$ and antibonding $E_g(v\pi)$ orbitals. The available orbitals, after σ-bonding, are in order of stability, $(E_u{}^b)[(B_{2g})(B_{2u})(E_u{}^a)(E_g{}^b)](E_g{}^a)$ the order within the square bracket being unknown, and there are 20 electrons, just enough to fill all available orbitals and thereby ensure diamagnetism. Since all the antibonding orbitals, as well as the bonding ones, are filled, we expect no double-bond character in either the Co–O or the O–O bonds, and the ion should not be appreciably destabilised by departure from linearity. Oxidation must involve removal of an electron from the least stable orbital which is $E_g{}^a$ and presumably concentrated mainly on the $O_2$ group, so that the resulting cation (II) is perhaps more correctly represented as $[(NH_3)_5Co^{III}{\cdot}\overset{1-}{O}_2{\cdot}Co^{III}(NH_3)_5]$ rather than as $[(NH_3)_5Co^{IV}{\cdot}\overset{2-}{O}_2{\cdot}Co^{III}(NH_3)_5]$. We expect the O–O and Co–O distances to be slightly shorter than in (I). The O–O distance should be about the same as that,

1·28 ± 0·07 Å, in the alkali "tetroxides" $M_2O_4$ which have been shown to contain the odd univalent anion $[O{\cdot}O]^-$ (Kassatochkin and Kotov, *J. Chem. Phys.*, 1936, **4**, 458).

*Iron Enneacarbonyl.*—Iron enneacarbonyl, $Fe_2(CO)_9$, differs from the previous binuclear compounds in that direct metal-to-metal bonding is possible. Owing to the large number of orbitals of the same symmetry type, the assignment of electrons to the various orbitals cannot be made unambiguously. A simplified treatment yields quite interesting results however. After σ-bonding there are left three orbitals on each iron atom (corresponding to the triply degenerate $T_2$ orbitals of the octahedral group) which transform in $C_{3v}$ as $A_1 + E$. Considering the iron atoms as a pair, we have in $D_{3h} = C_{3v} \times i$, $(A_{1g}{}^b)(E_g{}^b)(E_u{}^a)(A_{1u}{}^a)$ in order of stability. The order follows from the fact that the orbitals making up the $E$ representations will not interact much, while the $A_1$ atomic orbitals will interact strongly with one another, stabilising $A_{1g}$ and destabilising $A_{1u}$ (Fig. 3). The ten electrons remaining after σ-bonding are assigned as $(A_{1g}{}^b)^2(E_g{}^b)^4(E_u{}^a)^4$ leading to diamagnetism and with net formation of an iron–iron bond, in accord with the observed Fe–Fe distance, 2·46 Å (Powell and Ewens, *J.*, 1939, 286).

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## 529. *The Condensation of* 1 : 3-*Dimethylindole with Hexane-*2 : 5-*dione and Heptane-*2 : 6-*dione.*

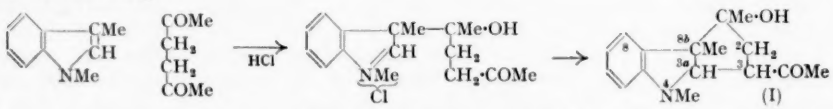
By SIR ROBERT ROBINSON and J. E. SAXTON.

The diketones named in the title couple with 1 : 3-dimethylindole in the β-position, and the resulting indoleninium salt then undergoes cyclisation between the indole α-carbon atom and the methylene carbon of an appropriately situated oxo-methylene group. This provides a laboratory model for the biosynthesis of strychnine from tryptamine or tryptophan in accordance with the earlier stages of R. B. Woodward's hypothesis.

THE αββ-trisubstituted dihydroindole system of strychnine can theoretically be constructed by condensation of a suitable dicarbonyl compound with tryptamine, provided that the β-position is attacked in the first phase of the reaction.

Experiments made in 1949 by Mr. B. P. Moore on the condensation of tryptophan with simple 1 : 5-dioxo-compounds gave unsatisfactory results in most cases, and the reason became clear from the work of the present authors on the similar condensation reactions of skatole (*J.*, 1950, 3136). The 1- and the 2-position were coupled with different carbonyl groups, and substituted benzopyrrocolines resulted. We suspected that the 1 : 2-attack should be attributed to ready coupling with the 1-position in the first place.

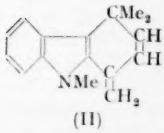
Hence it was decided to exclude this possibility by the use of 1 : 3-dimethylindole. Condensation with hexane-2 : 5-dione with the help of hydrogen chloride was not observed in anhydrous media but occurred readily in the presence of 10% of water. The product, $C_{16}H_{21}O_2N$, considered to be (I) is a dihydroindole derivative (ultra-violet spectrum and colour reactions). It contains hydroxyl and carbonyl groups (infra-red spectrum) and is a methyl ketone (iodoform reaction and derivatives). The course of the process is believed to be the following:




Another product of the reaction, best obtained under slightly varied conditions, was proved to be 1 : 4 : 9-trimethylcarbazole. It was also prepared from 1 : 4-dimethylcarbazole by treatment with sodamide and methyl iodide in liquid ammonia solution. The formation of this carbazole derivative indicates loss of the methyl in the 3-position

of the indole nucleus, presumably as methanol or methyl chloride; a normal condensation with loss of two molecules of water completes the process.

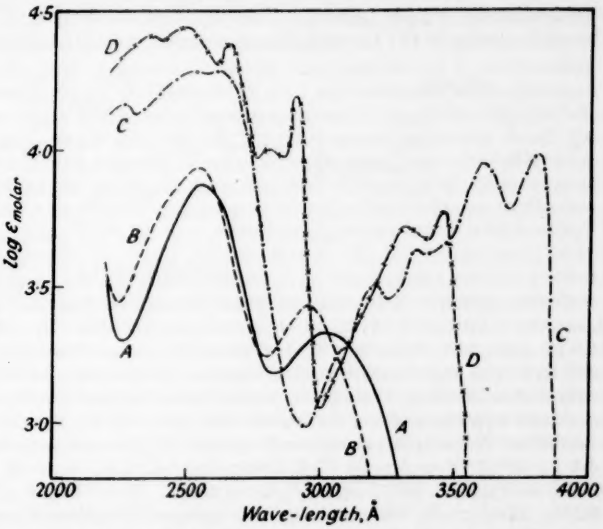
When the main product (I) was vigorously treated with hydrochloric acid it did not afford the trimethylcarbazole but changed to a substance, $C_{16}H_{17}N$, with loss of $2H_2O$. This is clearly an indole derivative and its ultra-violet spectrum (see Figure) discloses further conjugated unsaturation. The colour reactions, and the formation of a deeply coloured picrate, point in the same direction. One possible formula for this substance is (II) and there are two plausible alternatives which are *cyclo*heptatriene derivatives. The problem will be further studied and as the structure is not yet established discussion of the mechanism of its formation must be postponed.



(II)

It was important to extend this type of condensation to the homologous series and for this purpose the condensation of 1 : 3-dimethylindole and heptane-2 : 6-dione was studied.

The product was a feeble base, $C_{17}H_{21}ON$, which gave an oxidative colour reaction with ferric chloride very similar to that exhibited by strychnidine. The ultra-violet spectrum

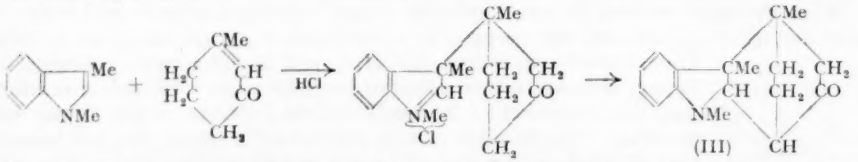



*A*, 3-*Acetyl*-1:2:3:3a:4:8b-*hexahydro*-1-*hydroxy*-1 : 4 : 8b-*trimethyl*cyclo*pent*[b]*indole in* MeOH.
*B*, 1:2:3:4:10:11-*Hexahydro*-1 : 9-*dimethylcarbazole in* MeOH.
*C*, *Indole*, $C_{16}H_{17}N$ (*m. p.* 134°), *in* cyclo*hexane*.
*D*, 1 : 4 : 9-*Trimethylcarbazole in* MeOH.

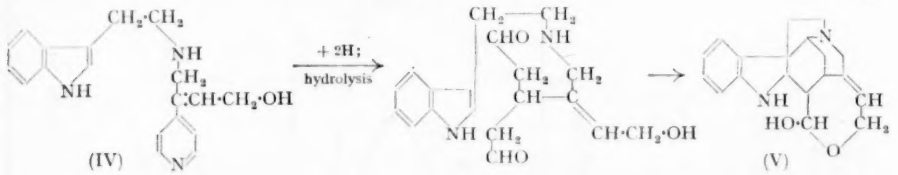
and other properties also proclaimed the dihydroindole nature of the substance. The course of the condensation was therefore analogous to that noted in the previous case but, if it were completely similar, the composition would have been $C_{17}H_{23}O_2N$. The new substance contains no hydroxyl group (infra-red spectrum) but it does contain a carbonyl group (infra-red spectrum and derivatives) which is not conjugated with a double bond. We naturally concluded that a substance of type (I) with an extra methylene group in the ring had suffered loss of water with formation of a double bond. However, further work cast doubt on this simple assumption. In the first place a double bond could not be characterised by catalytic reduction and, secondly, the iodoform reaction was either not exhibited or was uncertain. A direct comparison of the compounds $C_{16}H_{21}O_2N$ and $C_{17}H_{21}ON$ in the latter respect was carried out by grinding small specimens with a crystal of iodine, covering them with 10% sodium carbonate solution, and heating them side by side in a shallow bath of boiling water. Visible iodoform was produced from the $C_{16}$ compound but only a doubtful odour from the $C_{17}$ substance. The estimation of *C*-Me gave strong support to the conclusion that a methyl ketone group was absent.

When we realised that the structure (III) for the compound $C_{17}H_{21}ON$ accommodated the facts it seemed probable that the reaction involved dehydration of the diketone to methyl*cyclo*hexenone in the first instance. This hypothesis was confirmed by the formation of the compound $C_{17}H_{21}ON$ from 1 : 3-dimethylindole and 3-methyl*cyclo*hex-2-enone under

the usual conditions. The second phase of the process parallels that which occurs in the lower homologous series.




The investigation now described realises laboratory analogies for two fundamental steps of the biogenesis of strychnine proposed by R. B. Woodward (*Nature*, 1948, **162**, 155) but this has only been achieved by blocking the substitution of hydrogen on the indole nitrogen. Nevertheless a stereochemical device might be used to effect the same purpose. For example a pendent pyridine group could be employed; this by addition of two hydrogen atoms to the pyridine nucleus and hydrolysis would afford a substituted glutardialdehyde of the correct structure. Thus the synthesis of strychnine might be accomplished in an extraordinarily simple fashion. The pyridine derivative (IV) should yield the Wieland–Gumlich aldehyde (V) through the two stages indicated above.




## Experimental

*Condensaton of* 1 : 3-*Dimethylindole with Hexane*-2 : 5-*dione*. (A) 3-*Acetyl*-1 : 2 : 3 : 3a : 4 : 8b-*hexahydro*-1-*hydroxy*-1 : 4 : 8b-*trimethyl*cyclo*pent*[b]*indole** (I).—A mixture of 1 : 3-dimethylindole (2·9 g.), hexane-2 : 5-dione (2·5 g.), ethanol (9 c.c.), and water (1 c.c.) was cooled in ice, saturated with hydrogen chloride, and kept for 90 min. Water (50 c.c.) was added and the neutral material extracted with ether. The basic product was liberated from the aqueous solution by addition of dilute aqueous sodium hydroxide and isolated by means of ether. The cyclo*pentindole* crystallised from light petroleum (b. p. 60—80°) as massive, colourless rhombs, m. p. 90—92° (3·1 g., 58%) (Found: C, 73·6, 73·8; H, 8·2, 8·4; N, 5·45; active H, 0·82; NMe, 4·12; *C*-Me, 12·0%; *M*, 247. $C_{16}H_{21}O_2N$ requires C, 74·1; H, 8·1; N, 5·4; 2H, 0·77; 1NMe, 11·2; 3*C*-Me, 17·4%; *M*, 259). The *picrate*, prepared in ethanol, separated from acetone as yellow octahedra, m. p. 151° (decomp.) with darkening above 140° (Found: C, 54·2; H, 5·1. $C_{16}H_{21}O_2N,C_6H_3O_7N_3$ requires C, 54·1; H, 4·9%). The *semicarbazone* crystallised from ethanol as long, colourless prisms, m. p. 208—209° (Found: C, 64·4; H, 7·3; N, 18·2. $C_{17}H_{24}O_2N_4$ requires C, 64·6; H, 7·6; N, 17·7%). The base is rapidly degraded by concentrated aqueous hydrochloric acid (see below) but is quite stable to alkalis. It exhibits the properties of a tertiary aromatic amine, and gives a deep orange-red colour with ferric chloride. It gives iodoform with iodine and sodium carbonate solution, condenses with piperonaldehyde to a yellow piperonylidene derivative, and gives a brownish-red colour with sodium nitroprusside in aqueous methanolic sodium hydroxide solution.

The infra-red spectrum shows the presence of an unconjugated carbonyl group with a band at 5·85 μ, and a hydroxyl band at 2·82 μ. However, the base did not react with phenyl *iso*cyanate at room temperature in 72 hr., nor did it react with nitromethane in methanol. Acetic anhydride and pyridine in the cold did not affect the base, but the same reagent at the b. p. led to decomposition, as did the use of toluene-*p*-sulphonyl chloride in pyridine.

The ultra-violet absorption of the base was typical of a dihydroindole, with maxima at 2550 ($\log_{10} \varepsilon_{molar} = 3·97$) and 3000 Å ($\log_{10} \varepsilon_{molar} = 3·33$), which follows closely the absorption of hexahydro-1 : 9-dimethylcarbazole, which has maxima at 2550 ($\log_{10} \varepsilon_{molar} = 3·93$) and 2950 Å ($\log_{10} \varepsilon_{molar} = 3·42$).

3-*Acetyldodecahydro*-1-*hydroxy*-1 : 4 : 8b-*trimethyl*cyclo*pent*[b]*indole*.—The foregoing pentin-

* Enumeration and name according to Ring Index no. 1418.

dole (1·2 g.) in ethanol (25 c.c.) was hydrogenated at atmospheric pressure and temperature, Adams's catalyst (0·1 g.) being used. After 4 hr. only 100 c.c. of hydrogen had been absorbed, but after perchloric acid (1 drop of 60%) had been added the reduction continued. When absorption ceased 360 c.c. hydrogen had been taken up (336 c.c. for $3H_2$). The resulting solution was filtered, an excess of dilute alkali added, and the ethanol removed. The base was dissolved in ether, the solution dried, and the product obtained by distillation. The *decahydropentindole* (1 g.) was collected at 120—130°/0·05 mm. (Found: C, 72·8; H, 10·4; N, 4·9. $C_{16}H_{27}O_2N$ requires C, 72·5; H, 10·2; N, 5·3%). This base did not exhibit the colour reactions of the parent compound, for example, the oxidative reaction with ferric salts.

1 : 2 : 3 : 3a : 4 : 8b-*Hexahydro*-1-*hydroxy*-1-1′-*hydroxyethyl*-1 : 4 : 8b-*trimethyl*cyclo*pent*[b]-*indole*.—A solution of lithium aluminium hydride (0·3 g.) in ether (25 c.c.) was added dropwise to a solution of the acetylhexahydropentindole (1 g.) in ether (25 c.c.) and the mixture refluxed for an hour. The excess of the reagent was destroyed by addition of moist ether and then water; the ethereal layer was dried and evaporated. The residue was crystallised from benzene, and 1 : 2 : 3 : 3a : 4 : 8b-*hexahydro*-1-*hydroxy*-3-1′-*hydroxyethyl*-1 : 4 : 8b-*trimethyl*cyclo*pent*[b]*indole* (yield almost quantitative) obtained as long, colourless prisms, m. p. 142·5—143·5° (Found: C, 73·3, 73·9; H, 8·5, 8·8; N, 5·3. $C_{16}H_{23}O_2N$ requires C, 73·6; H, 8·8; N, 5·4%). This base is unaffected by boiling concentrated hydrochloric acid (10 min.), conditions under which the parent keto-amine is degraded to a compound $C_{16}H_{17}N$ (see below).

*Reaction of* 1 : 3-*Dimethylindole with Acetonylacetone* (B).—A solution of 1 : 3-dimethylindole (12 g.) and hexane-2 : 5-dione (10 g.) in ethanol (25 c.c.) was saturated with hydrogen chloride while cooling in ice, then kept at the room temperature for 6 hr., after which it was poured into water (200 c.c.) and extracted with ether. The ethereal solution was dried, the solvent removed, the residue distilled, and the volatile material collected at 140—190°/0·07 mm. (8·4 g.). The distillate was passed in light petroleum (b. p. 60—80°) through an alumina column. Elution with the same solvent gave 1 : 4 : 9-*trimethylcarbazole* (0·5 g.), obtained from methanol–ethanol as colourless needles, m. p. 131—132°, alone or mixed with authentic 1 : 4 : 9-trimethylcarbazole (see below: m. p. 132°) (Found: C, 85·6; H, 7·2; N, 6·7. $C_{15}H_{15}N$ requires C, 86·1; H, 7·2; N, 6·7%). Further elution of the substances adsorbed on the alumina column yielded colourless, uncrystallisable oils, which did not give crystalline picrates and possibly contained tetramethylcarbazoles.

*Synthesis of* 1 : 4 : 9-*Trimethylcarbazole*.—A solution of 1 : 4-dimethylcarbazole (1·1 g.) in liquid ammonia (25 c.c.) was added dropwise to a solution of sodamide (from 0·13 g. of sodium) in liquid ammonia (25 c.c.). The mixture was stirred, and methyl iodide (2 g.) added cautiously. The ammonia was allowed to evaporate, and moist ether was added, followed by water and dilute hydrochloric acid. The ethereal layer was dried and the solvent removed. The residue was crystallised from ethanol. 1 : 4 : 9-Trimethylcarbazole (yield almost quantitative) was obtained as colourless needles, m. p. 132° (Found: C, 86·1; H, 7·2; N, 6·7%). This substance developed a dark green colour in a mixture of concentrated sulphuric and nitric acids. The *picrate* crystallised from benzene in red needles, m. p. 185—186° (Found: C, 57·5; H, 4·3. $C_{15}H_{15}N,C_6H_3O_7N_3$ requires C, 57·5; H, 4·1%). The infra-red spectra of the two specimens of trimethylcarbazole were identical in the region 4—14 $\mu$.

*Action of Hydrochloric Acid on* 3-*Acetyl*-1 : 2 : 3 : 3a : 4 : 8b-*tetrahydro*-1-*hydroxy*-1 : 4 : 8b-*trimethyl*cyclo*pent*[b]*indole*.—A solution of this pentindole derivative (3 g.) in concentrated hydrochloric acid (30 c.c.) was heated for 30 min. on the steam-bath. The cooled solution was diluted with water (100 c.c.) and extracted with ether. The ethereal solution was dried ($K_2CO_3$) and the solvent removed. Distillation of the residual oil gave 1 : 3-dimethylindole (picrate m. p. and mixed m. p. 143—144°) and a *product*, b. p. 130—150°/0·025 mm. (1 g.), which solidified on trituration with light petroleum and was obtained as colourless needles, m. p. 134° (mixed m. p. with 1 : 4 : 9-trimethylcarbazole, 110—115°), from methanol (Found: C, 85·7, 86·3; H, 7·7, 7·6; N, 6·3; NMe, 9·4; *C*-Me, 11·9. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6; N, 6·3; 1NMe, 13·0; 2*C*-Me, 13·4%). The *picrate* separated from benzene as black, lustrous needles, decomp. 197° (Found: C, 58·3, 58·6; H, 4·7, 4·7; N, 12·6. $C_{16}H_{17}N,C_6H_3O_7N_3$ requires C, 58·4; H, 4·4; N, 12·4%).

In further preparations this substance was purified by conversion of the crude oil into the picrate and regeneration from this derivative. It gave a very pale yellowish-green colour with Ehrlich's reagent in the cold, which became blue on heating. The colour change was reversible. Excess of hydrochloric acid gave a very deep green colour in the presence of *p*-dimethylaminobenzaldehyde. Its colourless methanolic solution exhibited an intense blue fluorescence which was destroyed by addition of mineral acid.

The infra-red spectrum of this substance has a small peak at 5·80 μ, and a large one at 11·59 μ.

*Reduction of the indole* $C_{16}H_{17}N$. The indole derivative $C_{16}H_{17}N$ (0·36 g.) was hydrogenated in ethanol solution at the atmospheric temperature and pressure in presence of Raney nickel (W7) as the catalyst. Absorption ceased when 120 c.c. of hydrogen had been absorbed (105 c.c. required for $3H_2$). The solution was filtered, the ethanol removed, and the basic material extracted from the residual oil. The basic *product* was a colourless oil, b. p. 145—150°/0·01 mm. (Found: C, 83·7; H, 9·8; *C*-Me, 14·1. $C_{16}H_{23}N$ requires C, 83·8; H, 10·0; 2*C*-Me, 13·1; 3*C*-Me, 19·6%). The *picrate* crystallised from ethanol as long, yellow needles, m. p. 131—132° (Found: C, 58·0; H, 5·7; N, 12·8. $C_{16}H_{23}N,C_6H_3O_7N_3$ requires C, 57·6; H, 5·7; N, 12·2%).

1 : 4-*Ethylene*-1 : 2 : 3 : 4 : 10 : 11-*hexahydro*-4 : 9 : 11-*trimethyl*-2-*oxocarbazole* (III).—(*a*) A solution of 1 : 3-dimethylindole (4 g.), heptane-2 : 6-dione (6 g.), and water (4 c.c.) in ethanol (20 c.c.) was cooled in ice, and saturated with hydrogen chloride. The mixture was kept for 2 days, then diluted with water (100 c.c.) and extracted with ether. The ethereal layer was dried and evaporated, leaving a pale brown viscous oil (7·9 g.). A solution of this oil in light petroleum (b. p. 60—80°) was passed through a column of alumina, and eluent collected in 20-c.c. fractions. The fractions yielding a crystalline solid on evaporation were combined, and the product recrystallised from light petroleum (b. p. 60—80°). 1 : 4-*Ethylene*-1 : 2 : 3 : 4 : 10 : 11-*hexahydro*-4 : 9 : 11-*trimethyl*-2-*oxocarbazole* (2·5 g., 35%) was obtained as long, colourless prisms, m. p. 120—122° (Found: C, 80·2; H, 8·4; N, 5·4; *C*-Me, 5·27. $C_{17}H_{21}ON$ requires C, 80·0; H, 8·2; N, 5·5; 1*C*-Me, 5·97%).

(*b*) An ice-cold solution of 1 : 3-dimethylindole (2·5 g.) and 3-methyl*cyclo*hex-2-enone (2·5 g.) in ethanol (10 c.c.) and water (2 c.c.) was saturated with hydrogen chloride. After being kept overnight at the room temperature, the mixture was poured into water (100 c.c.) and extracted with ether. The dried ethereal extract yielded on evaporation 1 : 4-ethylene-1 : 2 : 3 : 4 : 10 : 11-hexahydro-4 : 9 : 11-trimethyl-2-oxocarbazole, which crystallised spontaneously on cooling. Recrystallisation from light petroleum (b. p. 60—80°) gave prisms (1·9 g., 50%), m. p. 120—122°, alone and when mixed with the product from 1 : 3-dimethylindole and heptane-2 : 6-dione (Found: C, 79·8; H, 8·3%). The *semicarbazone* separated from ethanol in rhombs, m. p. 205° (Found: C, 68·9; H, 8·0. $C_{18}H_{24}ON_4$ requires C, 69·2; H, 7·7%).

This substance is a weak base, which behaves in all respects like a dihydroindole. The ferric chloride oxidative colour reaction is intense carmine, while the Ehrlich reagent gives an emerald-green colour which slowly becomes deep blue. The base couples with diazonium salts to azo-dyes and gives a yellow 2 : 4-dinitrophenylhydrazone. It is soluble in an excess of 1% hydrochloric acid, sparingly so in 2% acid, and does not afford a picrate under the usual conditions.

In the infra-red region there is an absorption maximum at 5·82 μ, indicating an unconjugated carbonyl group; there is no band due to hydroxyl, nor any indication of an olefinic double bond.

The substance was not reduced at atmospheric temperature and pressure at palladised strontium carbonate or Raney nickel. It was reduced slowly in the presence of Adams's catalyst and ethanolic perchloric acid but, when absorption of hydrogen ceased, 25% of the base was recovered unchanged. The remaining fraction, which was strongly basic, was an uncrystallisable oil, which showed no absorption in the carbonyl region, and two small peaks in the hydroxyl region at 3·0 and 3·1 μ. The colour reactions of the product indicated that it still contained a dihydroindole system, and the absorption of hydrogen could be accounted for on the assumption that reduction of an oxo-group was the only reaction.

The ultra-violet spectrum of the parent substance, $C_{17}H_{21}ON$, was normal for a dihydroindole, the absorption showing maxima at 2550 ($\log_{10}\varepsilon = 3·89$) and 3030 Å ($\log_{10}\varepsilon = 3·48$).

This work was carried out during the tenure of an I.C.I. Fellowship (J. E. S.).

Dyson Perrins Laboratory, Oxford University. [*Received, April 8th,* 1953.]

## 530. *The Synthesis of Long-chain αω-Dihalides by Means of Acetylenic Compounds.*

By A. W. Nineham.

Methods are outlined whereby members of the series of straight-chain polymethylene dihalides can be synthesised through acetylenic intermediates with relative ease and in considerable quantities. Appropriate examples of previously inaccessible dihalides have been studied experimentally.

Published methods for the preparation of straight-chain polymethylene compounds are often unsatisfactory, particularly when the chain is of considerable length or when the compound is required in quantity. Few attempts have been made to use acetylenic compounds: only recent work such as the synthesis of vaccenic acid (Ahmad and Strong, *J. Amer. Chem. Soc.*, 1948, **70**, 1699, 3391) and of linoleic acid (Raphael, *J.*, 1950, 115, 120) has employed triply-bonded intermediates (see also Taylor and Strong, *J. Amer. Chem. Soc.*, 1950, **72**, 4263; Lumb and Smith, *J.*, 1952, 5032). The present work concerns the preparation of polymethylene dihalides by various reactions involving acetylenic bonds. The reactions studied seem perfectly general and lead to any member of the series with more than six carbon atoms from readily available starting materials in workable and often excellent yields. For summaries of the synthetic methods previously used for these dihalides see von Braun and Kamp (*Ber.*, 1937, **70**, 973) and Ziegler and Weber (*ibid.*, p. 1275).

The dihalides employed as starting materials in the present work are either the commercially available lower members or are derived from naturally occurring long-chain compounds, in particular, octamethylene and decamethylene dihalides from sebacic acid. Hexamethylene dibromide has been produced commercially from propargyl alcohol through hexa-2 : 4-diyne-2 : 6-diol, a single previous use of the methods to be described:

$$2HC{\equiv}C{\cdot}CH_2{\cdot}OH \longrightarrow (HO{\cdot}CH_2{\cdot}C{\equiv}C{\cdot})_2 \longrightarrow HO{\cdot}[CH_2]_6{\cdot}OH \longrightarrow Br{\cdot}[CH_2]_6Br$$

The acetylenic condensations have followed the technique described by Vaughn *et al.* (*J. Org. Chem.*, 1937, **2**, 1) and others. In general, it has been advantageous to employ 2—2·2 times the calculated amount of sodamide in the liquid ammonia condensations, whereby the product is obtained purer and in better yield. The acetylenic ethers are hydrogenated smoothly in the presence of Adams's platinum oxide catalyst at room temperature and pressure. In the case of 1-ethoxy-9-*o*-methoxyphenoxynon-3-yne it was desirable to carry out semi-hydrogenation with a palladium catalyst first. Finally, fission was carried out in open vessels for periods which increased with the length of the carbon chain.

The general synthetic procedures are classified as follows:

(i) A halogeno-ether (II) (cf. Ziegler and Weber, *loc. cit.*; Ziegler, Weber, and Gellert, *Ber.*, 1942, **75**, 1715) is treated with sodium acetylide, to give an ω-(methoxyphenoxy)acetylene (III) which is treated as the sodium salt with a further halogeno-ether, to give the acetylenic diether (IV) which is finally hydrogenated to (V) and converted into the dihalide:

$$\underset{\text{(II)}}{RO{\cdot}[CH_2]_n{\cdot}Br} \longrightarrow \underset{\text{(III)}}{RO{\cdot}[CH_2]_n{\cdot}C{\equiv}CH} \xrightarrow{RO{\cdot}[CH_2]_m{\cdot}Br} \underset{\text{(IV)}}{RO{\cdot}[CH_2]_n{\cdot}C{\equiv}C{\cdot}[CH_2]_m{\cdot}OR} \longrightarrow$$

$$\underset{\text{(V)}}{RO{\cdot}[CH_2]_{n+m+2}{\cdot}OR} \longrightarrow Br{\cdot}[CH_2]_{n+m+2}{\cdot}Br \qquad (R = o\text{- or } p\text{-methoxyphenyl})$$

The procedure has been illustrated for $n = m = 5$, to give dodecamethylene dibromide and di-iodide, and for $n = 2$, $m = 5$, to give nonamethylene di-iodide. An ethoxy-group was used for protection in the latter case because 2-ethoxyethyl bromide was available, but certain precautions became necessary during hydrogenation. An attempt to prepare 4-*o*-methoxyphenoxybutyne from 2-*o*-methoxyphenoxyethyl bromide and sodium acetylide gave only *o*-methoxyphenyl vinyl ether (cf. Summers and Larson, *J. Amer. Chem. Soc.*, 1952, **74**, 4498).

(ii) When the required dihalide contains $2n$ methylene groups and the dihalide with

$n - 2$ methylene groups is available, the acetylene (VI) can be coupled with itself in the presence of an oxidising agent to give a diacetylenic diether (VII), which is then hydrogenated and hydrolysed as before:

$$\underset{\text{(VI)}}{2RO\cdot[CH_2]_{n-2}\cdot C{:}{:}CH} \longrightarrow \underset{\text{(VII)}}{(RO\cdot[CH_2]_{n-2}\cdot C{:}{:})_2} \longrightarrow RO\cdot[CH_2]_{2n}\cdot OR \longrightarrow Br\cdot[CH_2]_{2n}\cdot Br$$

Several of the coupling methods described in the literature were applied to 7-*o*-methoxyphenoxyhept-1-yne. When the cuprous salt was heated with aqueous cupric chloride for some hours, 1 : 14-di-*o*-methoxyphenoxytetradeca-6 : 8-diyne was obtained (cf. Strauss and Kollek, *Ber.*, 1926, **59**, 1680), but shaking the acetylene in oxygen with aqueous alcoholic cuprous chloride and ammonium chloride (Bowden, Heilbron, Jones, and Sargent, *J.*, 1947, 1579) was not effective, perhaps owing to the very low solubility of the acetylene in the medium. No diyne was detected in an attempt to couple two molecules of 7-*o*-methoxyphenoxyhept-1-ynylmagnesium bromide with iodine, but 19% of a product, in which the acetylenic hydrogen had been replaced by iodine, was obtained.

(iii) Di-iodides and two mols. of sodium acetylide give αω-diacetylenes (VIII), which with two mols. of ω-bromoalkyl ethers give diacetylenes (IX), which are then treated in the usual way:

$$I\cdot[CH_2]_n\cdot I + 2HC{:}{:}CNa \longrightarrow \underset{\text{(VIII)}}{HC{:}{:}C\cdot[CH_2]_n\cdot C{:}{:}CH} \xrightarrow[NaNH_2]{Br\cdot[CH_2]_m\cdot OR}$$

$$RO\cdot[CH_2]_m\cdot C{:}{:}C\cdot[CH_2]_n C{:}{:}C\cdot[CH_2]_m\cdot OR \xrightarrow{2\ \text{Steps}} Br\cdot[CH_2]_{2m+n+4}\cdot Br$$
$$\text{(IX)}$$

This method is useful in the preparation of higher members of the series. For example, octamethylene dibromide was converted into octadecamethylene dibromide.

(iv) The converse procedure of (iii) was also used, in which two mols. of the sodium salt of an acetylenic ether were condensed with a polymethylene di-iodide, and the diacetylene resulting hydrogenated as usual:

$$2RO\cdot[CH_2]_n\cdot C{:}{:}CH + I\cdot[CH_2]_m\cdot I \longrightarrow RO\cdot[CH_2]_n\cdot C{:}{:}C\cdot[CH_2]_m\cdot C{:}{:}C\cdot[CH_2]_n\cdot OR \xrightarrow{2\ \text{Steps}} Br\cdot[CH_2]_{2n+m+4}\cdot Br$$

In this way, pentamethylene di-iodide and 7-*o*-methoxyphenoxyheptyne were converted into pentadecamethylene dibromide. An improved preparation of pentamethylene di-iodide is also described.

It will be seen that syntheses embodying one of these four procedures can easily be devised for any polymethylene compound from seven methylene groups upwards. Taylor and Strong (*loc. cit.*), however, discovered unexpected limitations in an analogous attempted synthesis of petroselinic acid.

Larger-scale working has been realised without difficulty in the preparation of 500 g. of dodecamethylene di-iodide.

Dithiuronium picrates obtainable from various dihalides are listed on p. 2606.

## Experimental

5-o-*Methoxyphenoxypentyl Bromide*.—Pentamethylene dibromide (920 g., 4 mols.), guaiacol (124 g., 1 mol.) and methanolic 2·7N-potassium hydroxide (380 c.c.) were heated on a steam-bath for 2 hr. The potassium bromide which crystallised was filtered off and the methanol distilled off at atmospheric pressure, followed by excess of pentamethylene dibromide at 120°/10 mm. The remaining oil was decanted from further potassium bromide which had separated, and was distilled in a high vacuum, giving 5-o-*methoxyphenoxypentyl bromide*, b. p. 125—128°/0·4 mm., $n_D^{20}$ 1·541 (206 g., 76% based on the guaiacol used). A refractionated portion of the product, b. p. 130—131°/0·45 mm., was analysed (Found: Br, 29·0. $C_{12}H_{17}O_2Br$ requires Br, 29·3%). The compound was characterised as the *thiuronium picrate*, obtained by heating 1 c.c. under reflux with thiourea (2 g.) in ethanol for 3 hr. and treating the hot solution with picric acid (1 g.) in ethanol (10 c.c.); the picrate crystallised in bright yellow prisms, m. p. 146° (Found: N, 14·1; S, 6·6. $C_{19}H_{23}O_9N_5S$ required N, 14·1; S, 6·4%).

7-o-*Methoxyphenoxyhept*-1-*yne*.—Sodium (50 g., >2 mols.) was converted into a suspension of sodium acetylide in liquid ammonia (2 l.) in the presence of a little ferric nitrate (cf. *inter al.*, Heilbron, Jones, and Weedon, *J.*, 1945, 83), and the stirred suspension was treated dropwise during 1½ hr. with 5-*o*-methoxyphenoxypentyl bromide (276 g., 1 mol.) in twice its bulk of dry

ether. Ether was added to replace the liquid ammonia lost by evaporation and the whole allowed to warm to room temperature overnight. It was finally heated gently under reflux on the steam-bath for 1½ hr., filtered, and washed with ether, and the solvent was evaporated, to give a thick oil, which gave fractions boiling at 130—152°/1 mm., and at 153—165°/1 mm. The main (lower-boiling) fraction solidified to a waxy *ether* which crystallised (141 g.) from light petroleum (b. p. 40—60°), m. p. 33°. The purer material distilled at 120—130°/0·2 mm. (Found: C, 76·9; H, 8·3; OMe, 14·4. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·2; OMe, 14·2%) and gave a silver salt on admixture with ammoniacal silver nitrate solution. The higher-boiling fraction, redistilled through a Vigreux column, gave 95 g. of 5-*o*-methoxyphenoxypentyl bromide. The average yield of a number of runs was 93%. The *mercury* salt was obtained by adding an alcoholic solution to potassium mercuri-iodide solution. It crystallised from benzene containing a little light petroleum (b. p. 40—60°) in colourless plates, m. p. 91—92° (Found: Hg, 31·6. $C_{28}H_{34}O_4Hg$ requires Hg, 31·6%).

1 : 12-*Di*-o-*methoxyphenoxydodec*-6-*yne*.—Sodamide (from 14 g. of sodium) in liquid ammonia (1·5 l.) was treated with 7-*o*-methoxyphenoxyhept-1-yne (125 g. in twice its bulk of dry ether) during 1 hr., with stirring, which was continued for a further hour, and then 5-*o*-methoxyphenoxypentyl bromide (157 g. in twice its volume of dry ether) was run in during 30 min. The reactants were stirred overnight and then the suspension was heated under reflux for 4 hr. After filtration, the ether was removed. The solid residue, crystallised from ethanol, gave 1 : 12-*di*-o-*methoxyphenoxydodec*-6-*yne* (245 g., 100%) as plates, m. p. 82·5—83°, showing no reaction for halogen or a free ethynyl group (Found: C, 75·8; H, 8·2; OMe, 15·0. $C_{26}H_{34}O_4$ requires C, 76·1; H, 8·3; OMe, 15·2%).

1 : 12-*Di*-o-*methoxyphenoxydodecane*.—1 : 12-Di-*o*-methoxyphenoxydodec-6-yne (226·5 g.) in ethyl acetate (800 c.c.) was shaken with Adams's platinum oxide (4 g.) in hydrogen at 4 atm. (theoretical uptake in 84 min.). The solution was filtered and evaporated. 1 : 12-*Di*-o-*methoxyphenoxydodecane* (186 g., 82%) was obtained as needles, m. p. 84—85°, after two recrystallisations of the residue from ethanol (Found: C, 75·1; H, 9·3. $C_{26}H_{38}O_4$ requires C, 75·4; H, 9·2%).

*Dodecamethylene Dibromide*.—1 : 12-Di-*o*-methoxyphenoxydodecane (5 g.) was heated under reflux with 50% aqueous hydrobromic acid (15 c.c.) for 48 hr. The cooled dark solution was made alkaline to litmus, extracted with benzene, black humus-like material being filtered off ("Hyflo supercel"), and the extract was dried and evaporated. The resulting oil solidified on trituration with a little very cold methanol and was then crystallised twice from methanol. Colourless waxy crystals of dodecamethylene dibromide (3·4 g., 86%), m. p. 38·5° (lit., m. p. 40·5—41°), were obtained (Found: C, 44·4; H, 7·6. Calc. for $C_{12}H_{24}Br_2$: C, 43·9; H, 7·3%).

*Dodecamethylene Di-iodide*.—This was prepared by heating the above diether for 16 hr. with 55% hydriodic acid, and the crude oil, in chloroform solution, was washed with solutions of sodium hydrogen sulphite and sodium hydroxide and dried before distillation. The product, b. p. 192—198°/0·5 mm., solidified. Crystallised from ethanol, it had m. p. 41° (90%) (lit., m. p. 41°).

1 : 14-*Di*-o-*methoxyphenoxytetradeca*-6 : 8-*diyne*.—(i) A solution of 7-*o*-methoxyphenoxyhept-1-yne (28·3 g. 0·13 mol.) in methanol (100 c.c.) was added to freshly prepared cuprous chloride (26 g.) in 50% ammonia solution (*d* 0·88; 50 c.c.) with stirring. A thick pea-green flocculent precipitate of the copper salt was formed, which was kept for 5 min., then filtered through sintered glass and washed with water, ethanol, and ether. The damp solid (32 g.) was suspended in aqueous ethanol (1 : 1) and heated on the steam-bath with cupric chloride (18 g.) in water (40 c.c.) for 48 hr. Another 5 g. of cupric chloride were added after 24 hr. The mixture was filtered, the residue was extracted thoroughly with hot methanol; the combined aqueous-alcoholic solutions crystallised on cooling. The residue was further digested with chloroform, and the dried chloroform solution was evaporated; the resulting oil partly crystallised; these crystals were added to the main product which was recrystallised from methanol. 1 : 14-*Di*-o-*methoxyphenoxytetradeca*-6 : 8-*diyne* (12·4 g., 71% calc. on the hept-1-yne not recovered) was obtained in colourless needles, m. p. 71°, which slowly assumed a deep violet colour, removed by recrystallisation [Found: C, 77·4; H, 7·9; OMe, 14·3%; *M* (in acetone), 405. $C_{28}H_{34}O_4$ requires C, 77·4; H, 7·8; OMe, 14·3%; *M*, 434]. The residual oil from the chloroform extract yielded 10·8 g. of 7-*o*-methoxyphenoxyhept-1-yne, b. p. 140—145°/0·4 mm.

(ii) Shaking a suspension of the copper salt of 7-*o*-methoxyphenoxyhept-1-yne and ammonium chloride in aqueous acetone in a hydrogenation apparatus filled with oxygen led to no uptake of oxygen, and an almost quantitative recovery of starting material.

(iii) Ethylmagnesium bromide solution, prepared from magnesium (2·4 g., 0·1 mol.),

ethyl bromide (10 c.c.), and dry ether (100 c.c.), was treated dropwise with 7-*o*-methoxyphenoxyhept-1-yne (21·8 g., 0·1 mol.) in dry ether (100 c.c.). After a few min., a colourless precipitate began to separate, and ethane was evolved. When the reaction was over, dry benzene (100 c.c.) was added, the ether distilled off, and the suspension of partly dissolved Grignard complex treated with iodine (12·7 g., 0·05 mol.) in benzene (100 c.c.), and stirring continued subsequently for a few min. The solution was kept overnight and decomposed with 1% sulphuric acid. The benzene layer was washed with sodium hydrogen carbonate solution and water, dried, and evaporated. The residual oil was distilled, giving fractions, b. p. 110—115°/0·01 mm. and 130—150°/0·01 mm. The former solidified on trituration with light petroleum (b. p. 40—60°) cooled in solid carbon dioxide and proved to be starting material (12·3 g.). The second fraction solidified on trituration with methanol similarly cooled and recrystallised from methanol in colourless prisms, m. p. 62° (6·6 g.). It appeared from the analytical data and the absence of any precipitate with ammoniacal silver nitrate solution, to be 1-*iodo*-7-*o*-*methoxyphenoxyhept*-1-*yne* [Found: C, 48·7; H, 5·1; I, 37·2; OMe, 9·5%; *M* (in acetone), 318. $C_{14}H_{17}O_2I$ requires C, 48·8; H, 4·9; I, 36·9; OMe, 9·1; *M*, 344].

1 : 14-*Di*-*o*-*methoxyphenoxytetradecane*.—1 : 14-Di-*o*-methoxyphenoxytetradeca-6 : 8-diyne (5·75 g.) was hydrogenated in dry ethyl acetate (50 c.c.) with Adams's platinum oxide (0·5 g.) at room temperature and pressure (100% uptake in 8 hr.). The solution was filtered hot, and colourless 1 : 14-*di*-*o*-*methoxyphenoxytetradecane* (5·3 g., 92%) crystallised, having m. p. 81—82° (from ethanol) (Found: C, 76·0; H, 9·2; OMe, 13·8. $C_{28}H_{42}O_4$ requires C, 76·0; H, 9·5; OMe, 14·0%).

*Tetradecamethylene Dibromide*.—This was obtained as a colourless wax (40%), m. p. 48°, (from methanol) (lit., m. p. 49—49·5°), after the above diether had been heated with 50% hydrobromic acid and acetic anhydride for 70 hr.

*Tetradecamethylene Di-iodide*.—Treatment of 1 : 14-di-*o*-methoxyphenoxytetradecane (10 g.) with 55% hydriodic acid (100 c.c.) for 24 hr. (as above) gave an oil, b. p. 200—220°/0·8 mm., which solidified, giving *tetradecamethylene di-iodide*, plates (from methanol), m. p. 50—51° (8·5 g., 82%) (Found: I, 56·0. $C_{14}H_{28}I_2$ requires I, 56·3%).

4-*Ethoxybutyne*.—2-Ethoxyethyl bromide (*Org. Synth.*, 1943, **23**, 32) was treated with sodium acetylide according to Kroeger and McCusker (*J. Amer. Chem. Soc.*, 1937, **59**, 213). It was characterised as the mercury salt, colourless prisms (from ethanol), m. p. 100·5° (lit., m. p. 99·5°) (Found: Hg, 50·8. Calc. for $C_{12}H_{18}O_2Hg$: Hg, 50·8%).

1-*Ethoxy*-9-*o*-*methoxyphenoxynon*-3-*yne*.—4-Ethoxybutyne (45 g., 0·45 mol.) in ether (100 c.c.) was run into a suspension of sodamide in liquid ammonia (1 l.) prepared from sodium (18 g., 0·8 mol.) and stirred for 1 hr. The suspended sodium salt was then treated with 5-*o*-methoxyphenoxypentyl bromide (93 g., 0·35 mol.) in ether (200 c.c.) during 2 hr. and the ammonia allowed to evaporate with stirring overnight. After 1 hour's heating under reflux the ethereal solution was filtered, the ether removed, and the residue distilled, first at the water-pump, and then in a high vacuum, giving fractions, (*a*) b. p. 40—50°/12 mm., 4-ethoxybutyne, (*b*) b. p. 150—180°/12 mm. (15 g.), (*c*) b. p. 200—210°/11 mm. (17 g.), and (*d*) b. p. 180—185°/0·1 mm. (45 g.). Redistillation of fractions (*b*), (*c*), and (*d*) through a short Vigreux column gave finally 53 g. (55%) of 1-*ethoxy*-9-*o*-*methoxyphenoxynon*-3-*yne* (b. p. 145—150°/0·05 mm., $n_D^{20}$ 1·516) which solidified at about 10—12°. A redistilled portion, b. p. 147—150°/0·05 mm., was analysed (Found: C, 75·0; H, 9·1; alkoxy-O, 11·6. $C_{18}H_{26}O_3$ requires C, 74·5; H, 9·0; alkoxy-O, 11·0%).

1-*Ethoxy*-9-*o*-*methoxyphenoxynonane*.—Some difficulty was experienced in hydrogenation of the above acetylene because of the tendency to hydrogenolysis of the ethoxy-group. Adams's platinum oxide in ethyl acetate, and 5% palladised barium sulphate in ethyl acetate, caused some dealkylation. Raney iron produced no hydrogen uptake. 1-Ethoxy-9-*o*-methoxyphenoxynon-3-yne (33 g.) in ethyl acetate (100 c.c.) was shaken in an atmosphere of hydrogen with 10% palladised calcium carbonate (1 g.) at room temperature and pressure. Hydrogen uptake was 47% after 2 hr. and then almost ceased. The catalyst was filtered off, Adams's platinum oxide (1 g.) added, and hydrogenation continued. A rapid uptake of another 43% occurred. The solution was filtered, the solvent evaporated, and the residue distilled, to give 1-*ethoxy*-9-*o*-*methoxyphenoxynonane* (30 g., 91%), as a viscous colourless oil, b. p. 210—214°/9 mm., which slowly crystallised (Found: C, 73·6; H, 9·8. $C_{18}H_{30}O_3$ requires C, 73·5; H, 10·1%). When the acetylene compound was hydrogenated in the presence of 5% palladised barium sulphate, 50% of the theoretical uptake of hydrogen was observed. After being worked up as before, the product distilled at 210—215°/16 mm., and analysis indicated that it was 1-*ethoxy*-9-*o*-*methoxyphenoxynon*-6-*ene*, which was confirmed by the strong colour reaction

with tetranitromethane, absent from tests with both the starting material and the fully reduced compound (Found: C, 74·1; H, 9·0. $C_{18}H_{28}O_2$ requires C, 74·0; H, 9·0%).

*Nonamethylene Di-iodide.*—1-Ethoxy-9-*o*-methoxyphenoxynonane (30 g.) was treated for 30 hr., with stirring, with 55% hydriodic acid (200 c.c.) and worked up in the usual way, giving *nonamethylene di-iodide*, b. p. 123°/0·2 mm., $n_D^{15}$ 1·560 (19·8 g., 74%), solidifying to a colourless wax, m. p. *ca.* 12—15° (Found: I, 66·1. $C_9H_{18}I_2$ requires I, 66·8%).

Hydrolysis for 24 hr. without stirring gave about 45% of nonamethylene di-iodide and about 50% of an oil, b. p. 185—187°/0·5 mm., probably 9-*o*-hydroxyphenoxynonyl iodide (Found: I, 36·7. Calc. for $C_{15}H_{23}O_2I$: I, 35·1%).

When an attempt to prepare 4-*o*-methoxyphenoxybutyne from sodium acetylide in liquid ammonia and 2-*o*-methoxyphenoxyethyl bromide was made (Di Boscogrande, *Atti R. Accad. Lincei*, 1897, [v], **6**, II, 33), the product, apart from some recovered starting material, appeared to be *o*-methoxyphenyl vinyl ether, b. p. 95—100°/10 mm., 200—202°/760 mm. (Found: C, 71·4; H, 6·9. Calc. for $C_9H_{10}O_2$: C, 71·9; H, 6·9%). No acetylenic reactions were observed.

3-p-*Methoxyphenoxypropyl Bromide.*—(*a*) By the procedure indicated for 5-*o*-methoxyphenoxypentyl bromide, 3-p-*methoxyphenoxypropyl bromide* was obtained as a colourless oil (64%), b. p. 178—180°/20 mm., 156—159°/10 mm., $n_D^{20}$ 1·5459 (Found: C, 49·8; H, 5·5; OMe, 12·9. $C_{10}H_{13}O_2Br$ requires C, 49·0; H, 5·3; OMe, 12·6%). Some fore-run, b. p. 157—175°/20 mm., m. p. 51—52°, was also obtained, identified as dimethylquinol, an impurity in the starting material. The residue from the distillation solidified and crystallised from methanol; 1 : 3-di-*o*-methoxyphenoxypropane was thereby obtained as colourless plates, m. p. 87° (lit., m. p. 88°) (Found: C, 71·3; H, 7·0; OMe, 22·0. Calc. for $C_{17}H_{20}O_4$: C, 70·8; H, 7·0; OMe, 21·5%).

(*b*) When *p*-methoxyphenol, trimethylene dibromide and aqueous sodium hydroxide were heated together overnight, only 36% of the pure product was obtained.

The halide was characterised by conversion into the *thiuronium picrate* which crystallised from ethanol in flat yellow plates or prisms, m. p. 147°, and sometimes in a mixture of yellow prisms and scarlet needles. The scarlet form, m. p. 148°, was also formed by cooling the yellow melt and appeared to be the metastable form since it reverted to the other after about two weeks (Found: N, 14·8; S, 7·0. $C_{17}H_{19}O_9N_5S$ requires N, 14·9; S, 6·8%).

5-p-*Methoxyphenoxypent*-1-*yne.*—3-*p*-Methoxyphenoxypropyl bromide (175 g.) was treated as already described with sodium acetylide (prepared from 40 g. of sodium in 1½ l. of liquid ammonia), and the resulting yellow oil was distilled. After a few drops of fore-run, b. p. 140—160°/19 mm., 5-p-*methoxyphenoxypent*-1-*yne* (131 g., 97%) was collected at 163—166°/19 mm. Redistilled through a 12-cm. Vigreux column, it had b. p. 151—155°/11 mm., m. p. 24° (Found: C, 75·5; H, 7·6; OMe, 16·8. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4; OMe, 16·3%). The residue from the first distillation gave a small amount of an unidentified *substance*, colourless plates (from methanol), m. p. 65°, depressed in m. p. in admixture with 1 : 3-di-*p*-methoxyphenoxypropane (m. p. 84°) (Found: C, 66·9; H, 8·0; OMe, 18·6%). 5-*p*-Methoxyphenoxyprop-1-yne was characterised as its *mercury* salt, crystallising from benzene in plates, m. p. 109—111° (Found: Hg, 34·7. $C_{24}H_{26}O_4Hg$ requires Hg, 34·7%).

1 : 15-*Di*-p-*methoxyphenoxypentadeca*-4 : 11-*diyne.*—Pentamethylene di-iodide was obtained by refluxing tetrahydropyran (250 c.c.) with 55% hydriodic acid (300 c.c.) for 8 hr., the lower layer being separated and washed with aqueous sodium hydrogen sulphite, sodium hydroxide, and water, and dried. After recovery of 70 c.c. of tetrahydropyran, the di-iodide, b. p. 155—157°/24 mm. (119 g.), was collected (lit., b. p. 149°/20 mm.).

5-*p*-Methoxyphenoxypent-1-yne (38 g.) was converted into the sodium salt in liquid ammonia (100 c.c.) and treated with redistilled pentamethylene di-iodide (25 g.) in ether (50 c.c.). After being stirred overnight, the ethereal suspension was refluxed for 6 hr. and then worked up as before. The red oil left after the removal of ether was distilled and after a fore-run of the acetylenic starting material (b. p. 160—165°/20 mm.) the residue was distilled in a high vacuum, and a thick oil, b. p. 220—240°/0·1 mm., was collected. This solidified. The 1 : 15-*di*-p-*methoxyphenoxypentadeca*-4 : 11-*diyne* (12·6 g., 40% based on the pentyne not recovered) recrystallised in prisms, m. p. 44·5° (Found: C, 77·9; H, 8·0; OMe, 14·2. $C_{29}H_{36}O_4$ requires C, 77·6; H, 8·0; OMe, 13·8%).

An alternative preparation in which pentamethylene dibromide was used led to the same product (mixed m. p.) but in very inferior yield. Compounds containing a small percentage of bromine were isolated from middle fractions of the distilled product in this case.

1 : 15-*Di*-p-*methoxyphenoxypentadecane.*—1 : 15-Di-*p*-methoxyphenoxypentadeca-4 : 11-diyne (12·6 g.) in ethyl acetate (50 c.c.) was hydrogenated at room temperature and pressure with Adams's platinum oxide (1 g.) (86% uptake in 2 hr.). The solution was filtered hot and

1 : 15-*di*-p-*methoxyphenoxypentadecane* crystallised. It recrystallised from methanol in needles, m. p. 87—88° (11·3 g., 90%) (Found : C, 75·7; H, 9·5; OMe, 14·1. $C_{29}H_{44}O_4$ requires C, 76·3; H, 9·6; OMe, 13·5%).

*Pentadecamethylene Dibromide.*—1 : 15-Di-*p*-methoxyphenoxypentadecane (4·6 g., 0·01 mol.) was refluxed in acetic anhydride (20 c.c.), after addition of 50% hydrobromic acid (20 c.c.), for 32 hr. After being worked up in the usual way, the oil was distilled, giving pentadecamethylene dibromide, b. p. 175—190°/14 mm., m. p. 26·5—27° (3·2 g., 87%) (Found : Br, 42·2. Calc. for $C_{15}H_{30}Br_2$ : Br, 43·2%), and a small amount of starting material, b. p. 235—240°/14 mm.

*Dodeca*-1 : 10-*diyne.*—To sodium acetylide, prepared from sodium (23 g., 1 atom) in liquid ammonia (1 l.), octamethylene dibromide (Luttringhaus and Schade, *Ber.*, 1941, **74**, 1565) (133 g., 0·5 mol.) was added in ether (100 c.c.) during 1 hr. with stirring. Ammonia was removed by stirring overnight, more ether (250 c.c.) was added, and the mixture heated under reflux for 3 hr. The filtered ethereal solution was washed with water, dried, and evaporated. The remaining oil was fractionated through a 5-cm. Vigreux column, giving fractions, (i) b. p. 110—114°/19 mm. and (ii) b. p. 114—150°/20 mm. Fraction (ii) appeared to be a mixture of brominated compounds. Fraction (i) was redistilled at 110°/19 mm. This product (45·5 g.) was slightly contaminated with halogenated material, but on being kept for some days at 0—10° crystallised, giving pure *dodeca*-1 : 10-*diyne*, m. p. 27°, very soluble in all organic solvents (Found : C, 87·8; H, 11·0. $C_{12}H_{18}$ requires C, 88·8; H, 11·2%).

In an attempt made to prepare the mercury salt, an amorphous white solid was obtained, which slowly darkened on heating and decomposed without melting between 150° and 250°. This was insoluble in most organic solvents except chloroform and carbon tetrachloride, in which it dissolved freely, and benzene, in which it dissolved with great difficulty and only separated again, during several days, after the addition of light petroleum (b. p. 40—60°). It was still amorphous and was dried in a vacuum-desiccator for a week. Analyses for mercury failed to give consistent values and it appeared that the product was non-homogeneous and possibly polymeric.

1 : 18-*Di*-p-*methoxyphenoxyoctadeca*-4 : 14-*diyne.*—Dodecadiyne (19·0 g.) in ether (50 c.c.) was run slowly into a suspension of sodamide [from sodium (5·4 g.) in liquid ammonia (500 c.c.)] and then stirred for 30 min. 3-*p*-Methoxyphenoxypropyl bromide (60 g.) in ether (100 c.c.) was then added dropwise with stirring, and the mixture stirred overnight whilst the ammonia evaporated. After 1½ hours' refluxing, the product was decomposed with dilute sulphuric acid, and the ethereal extract was separated, washed with aqueous sodium hydrogen carbonate and water and dried. After the removal of the ether, the residue partly solidified; it was triturated with methanol, giving 1 : 18-*di*-p-*methoxyphenoxyoctadeca*-4 : 14-*diyne* (14·3 g., 36%), m. p. 62·5—63·5° (from methanol) (Found : C, 78·6; H, 8·3; OMe, 12·9. $C_{32}H_{42}O_4$ requires C, 78·4; H, 8·6; OMe, 12·6%). The residual oil from the methanolic mother-liquors was distilled to give fractions, b. p. 117—119°/15 mm. (6·0 g.; dodecadiyne), 120—140°/15 mm., and 155—170°/15 mm. (*p*-methoxyphenoxypropyl bromide). The residue (2·2 g.) had m. p. 85—87° after crystallisation from light petroleum (b. p. 60—80°) and analysis and a mixed m. p. determination confirmed that this was 1 : 3-di-*p*-methoxyphenoxypropane.

1 : 18-*Di*-p-*methoxyphenoxyoctadecane.*—1 : 18-Di-*p*-methoxyphenoxyoctadeca-4 : 14-diyne (10 g.) in dry ethyl acetate (150 c.c.) in the presence of Adams's platinum oxide (1 g.) was hydrogenated at room temperature and pressure (100% uptake in 20 min.). The solution was

$NH_2{\cdot}(NH{:})C{\cdot}S{\cdot}[CH_2]_n{\cdot}S{\cdot}C(:NH){\cdot}NH_2,2C_6H_3O_7N_3$

| | | | | Found (%) | | | | Required (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *n* | Solvent | M. p. | Formula | C | H | N | S | C | H | N | S |
| 4 | A | 240—242° * | $C_{18}H_{20}O_{14}N_{10}S_2$ | 33·2 | 3·2 | 20·8 | — | 32·5 | 3·0 | 21·1 | — |
| 5 | B | 227—228 | $C_{19}H_{22}O_{14}N_{10}S_2$ | 33·8 | 3·3 | 20·0 | — | 33·7 | 3·3 | 20·6 | — |
| 6 | C | 243—245 * | $C_{20}H_{24}O_{14}N_{10}S_2$ | 34·8 | 3·9 | — | — | 34·6 | 3·5 | — | — |
| 7 | B | 228—229 * | $C_{21}H_{26}O_{14}N_{10}S_2$ | 35·2 | 3·8 | 19·4 | — | 34·8 | 3·8 | 19·4 | — |
| 8 | B | 206 | $C_{22}H_{28}O_{14}N_{10}S_2$ | 36·7 | 3·9 | 19·4 | — | 36·8 | 4·2 | 19·2 | — |
| 9 | D | 202—204 | $C_{23}H_{30}O_{14}N_{10}S_2$ | — | — | 19·0 | 9·0 | — | — | 19·0 | 8·7 |
| 10 | E | 211—212 * | $C_{24}H_{32}O_{14}N_{10}S_2$ | 39·2 | 4·5 | 18·4 | — | 38·5 | 4·3 | 18·7 | — |
| 12 | F | 183·5—184 | $C_{26}H_{36}O_{14}N_{10}S_2$ | 40·2 | 4·8 | 17·5 | 8·5 | 40·2 | 4·7 | 18·0 | 8·3 |
| 14 | B | 175—175·5 | $C_{28}H_{40}O_{14}N_{10}S_2$ | — | — | 17·1 | 8·0 | — | — | 17·4 | 8·0 |
| 15 | G | 143—145 | $C_{29}H_{42}O_{14}N_{10}S_2$ | — | — | 16·9 | — | — | — | 17·1 | — |
| 18 | B | 151·5—152·5 | $C_{32}H_{48}O_{14}N_{10}S_2$ | 44·8 | 5·7 | 16·2 | 7·4 | 44·7 | 5·6 | 16·3 | 7·4 |

* With decomp. A, Propylene glycol. B, Ethanol. C, Methanol. D, *iso*Propanol. E, Aqueous acetone (1 : 1). F, Aqueous methanol (3 : 1). G, Benzene.

filtered hot, and, on cooling, 1 : 18-*di*-p-*methoxyphenoxyoctadecane* (10·1 g., 99%) crystallised in plates, m. p. 123° (Found: C, 77·4; H, 10·1; OMe, 12·2. $C_{32}H_{50}O_4$ requires C, 77·1; H, 10·0; OMe, 12·4%).

*Octadecamethylene Dibromide.*—1 : 18-Di-*p*-methoxyphenoxyoctadecane (2·5 g.) was heated for 24 hr. under reflux with acetic anhydride (25 c.c.) after admixture with 50% hydrobromic acid (25 c.c.). After the usual working up, the residue solidified, giving octadecamethylene dibromide (1·82 g., 88%), m. p. 60·5—62·5° (from ethanol) (lit., m. p. 63·5—64°), which was characterised in the usual way.

*Dithiuronium Salts.*—The *alkylenedithiuronium picrates* (see Table), prepared in the usual way, formed yellow prisms, except that when $n = 6$ or 9 needles were obtained, and when $n = 18$ the crystal form was not identified.

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## 531. *Infra-red Absorptions of Vinyl and* iso*Propenyl Groups in Polar Compounds.*

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The characteristic olefinic absorptions of a number of polar allyl, vinyl, and *iso*propenyl compounds have been measured in solution, and new correlations established for the esters, ketones, and ethers. The correlations for acrylates and methacrylates include absorptions associated with the ester group.

Conjugation explains some of the shifts of $\nu_{C:C}$, but is not responsible for those of $\delta_{CH}$, for which no suitable models exist. An additivity rule is suggested and tested.

CHARACTERISTIC infra-red absorptions for vinyl and *iso*propenyl groups in hydrocarbon environment are well established (Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland, *J.*, 1950, 915; McMurray and Thornton, *Analyt. Chem.*, 1952, **24**, 318; Sheppard and Simpson, *Quart. Reviews*, 1952, **6**, 1) but little has been reported on the effect of polar substituents upon these absorptions apart from the vinyl halides (Thompson and Torkington, *J.*, 1944, 597) and allyl halides (*idem*, *Trans. Faraday Soc.*, 1946, **42**, 432).

The vibrational modes of the characteristic absorptions (Sheppard and Simpson, *loc. cit.*, give an excellent review of the nature of these absorptions) are $\nu_{C:C}$ (C:C stretching at *ca.* 1650 cm.$^{-1}$) and $\delta_{CH}$ (hydrogen deformation vibrations at *ca.* 1400 and 850—1000 cm.$^{-1}$). $\nu_{C:C}$ is primarily dependent upon the C:C stretching force constant and is therefore lowered by conjugation; its intensity (group molar absorptivity) should be increased by adjacent polar groups. The assignments of the $\delta_{CH}$ vibrations are fairly definite, but there is no suitable model which relates their frequencies to the conventional structural representation of the molecule.

### EXPERIMENTAL AND RESULTS

The materials used were mainly made and supplied by Dr. W. Cooper and Mr. E. Catterall. Spectra were all measured in "AnalaR" carbon tetrachloride (usually as 0·5M-solutions

TABLE 1. *Vinyl compounds*, $CH_2{:}CH{\cdot}X$.

| Compound | $\nu_{C:C}$, cm.$^{-1}$ | $\varepsilon$ | $\delta_{CH}$, cm.$^{-1}$ | $\varepsilon$ | $\delta_{CH}$, cm.$^{-1}$ | $\varepsilon$ | $\delta_{CH}$, cm.$^{-1}$ | $\varepsilon$ |
|---|---|---|---|---|---|---|---|---|
| *Allyl ethers* (X = $CH_2{\cdot}OR$) *and acetals* [$(CH_2{:}CH{\cdot}CH_2{\cdot}O)_2CHR$] | | | | | | | | |
| Diallyl ether | 1648 | 6 | 988 | 36 | 925 | 98 | N.I. | — |
| Diallyl formal | 1645 | 17 | 989 | 75 | 923 | 100 | 1420 | 20 |
| | | | | | | | 1404 | 18 |
| 1 : 1-Diallyloxybutane | 1644 | 20 | 991 | 90 | 921 | 97 | 1425 | 28 |
| | | | | | | | 1410 | 22 |
| 1 : 1 : 3-Triallyloxypropane | 1644 | ~15 | 989 | ~70 | 923 | ~85 | 1420 | ~25 |
| Summary | 1645 ± 2 | 6—20 | 989 ± 1 | 36—90 | 923 ± 2 | 85—100 | 1422 ± 3 | 20—28 |

TABLE 1.—*Continued.*

| Compound | $\nu_{C:C}$, cm.$^{-1}$ | ε | $\delta_{CH}$, cm.$^{-1}$ | ε | $\delta_{CH}$, cm.$^{-1}$ | ε | $\delta_{CH}$, cm.$^{-1}$ | ε |
|---|---|---|---|---|---|---|---|---|
| *Allyl esters* (X = $CH_2$·O·CO·R) | | | | | | | | |
| Adipate | 1650 | 27 | 986 | 100 | 932 | 100 | 1420 | 48 |
| | | | | | 923 (sh) | 84 | | |
| Sebacate | 1654 | 27 | 988 | 95 | 932 | 100 | 1423 | 45 |
| | | | | | 920 (sh) | 72 | | |
| Acrylate | (i) | — | 983 (i) | 135 (i) | 932 | 90 | (i) | — |
| | | | | | 921 | 75 | | |
| Methacrylate | (i) | — | 984 | 90 | 939 (i) | 140 (i) | 1420 | 45 |
| | | | | | 922 | 75 | | |
| Summary | 1652 ± 3 | ~27 | 985 ± 3 | 90—100 | 932 | 90—100 | 1421 ± 2 | 45—48 |
| | | | | | 922 ± 1 | 72—84 | | |
| *Vinyl ethers* (X = OR) | | | | | | | | |
| Ethyl | 1634 | 72 | 964 | 80 | 943 | 28 | N.I. | — |
| | 1608 | 112 | | | | | | |
| *n*-Butyl | 1632 | 65 | 960 | 55 | 942 | 33 | N.I. | — |
| | 1610 | 110 | | | | | | |
| *iso*Butyl | 1632 | 65 | 962 | 60 | 941 | 37 | N.I. | — |
| | 1608 | 110 | | | | | | |
| 2-Ethylhexyl | 1632 | 74 | 963 | 75 | 944 | 35 | N.I. | — |
| | 1610 | 122 | | | | | | |
| 2-Chloroethyl | 1640 | 65 | 960 | 80 | 941 | 40 | N.I. | — |
| | 1617 | 120 | | | | | | |
| Summary | 1634 ± 3 | 65—74 | 962 ± 2 | 55—80 | 942 ± 1 | 28—40 | N.I. | — |
| | 1611 ± 4 | 110—120 | | | | | | |
| *Vinyl esters* (X = O·CO·R) | | | | | | | | |
| Acetate | 1647 | 90 | 948 | 90 | 872 | 110 | N.I. | — |
| Benzoate | 1647 | 100 | 948 | 105 | 871 | 130 | N.I. | — |
| Crotonate | 1647 | 120 | 949 | 100 | 868 | 120 | N.I. | — |
| Summary | 1647 | 90—120 | 948 ± 1 | 90—105 | 870 ± 2 | 110—130 | N.I. | — |
| *Vinyl ketones* (X = CO·R) | | | | | | | | |
| Methyl | 1618 | ~90 | 983 | ~100 | 953 | ~120 | N.I. | — |
| Ethyl | 1619 | 48 | 984 | 68 | 955 | 85 | N.I. | — |
| Propyl | 1620 | ~55 | 982 | ~75 | 954 | ~65 | N.I. | — |
| Summary | 1619 ± 1 | 48—90 | 983 ± 1 | 68—100 | 954 ± 1 | 65—120 | N.I. | — |
| *Conjugated diolefins* (X = CR:CR′R″) [a] | | | | | | | | |
| $CH_2$:CH·CH:$CMe_2$ (API 453) | — | — | 994 | — | 893 | — | — | — |
| $CH_2$:CH·CMe:$CH_2$ (API 278) | — | — | 990 | — | ~910 | — | — | — |
| *cis*-$CH_2$:CH·CH:CHMe (API 496) | — | — | 998 | — | 908 | — | — | — |
| *trans*-$CH_2$:CH·CH:CHMe (API 497) | — | — | 1002 | — | 900 | — | — | — |
| $CH_2$:CH·CH:$CH_2$ (API 919) | — | — | 1014 | — | 909 | — | — | — |
| Summary | — | — | 1000 ± 9 | — | 904 ± 7 | — | — | — |
| *Miscellaneous* | | | | | | | | |
| X = $CH_2$·CN | 1645 | 26 | 984 | 57 | 928 | 68 | 1420 | 48 |
| X = CN | 1612 | 3·5 | 960 [b] | 78 | [b] | — | 1413 | 26 |
| | 1645 | 2·5 | | | | | | |
| X = CO·H | 1618 | — | 985 | — | 971 | — | N.I. | — |
| | | | | | 913 | | | |
| X = $CO_2$H | 1635 | 90 | 981 | 110 | 973 | 120 | N.I. | — |
| | 1615 | 70 | | | 930 [c] | 80 | | |
| X = $CH(OEt)_2$ | 1647 | ~5 | 986 | 125 | 935 | 96 | 1413 | 46 |
| X = CH(CN)·O·CO·Me | 1649 | — | 978 | — | 946 | — | 1418 | — |

*Notes to Tables* **1—3.**

N.I. Not investigated. (sh) Shoulder. (i) Interference from other olefinic groups.

[a] Published spectra; not in $CCl_4$. [b] Unresolved doublet (Thompson and Torkington, *J.*, 1944, 597). [c] Possibly the ~900-cm.$^{-1}$ acid band (Flett, *J.*, 1951, 962). [d] Insufficient data for correlation. [e] The mean frequency of the doublets is used to calculate the summary mean. [f] Methyl excepted.

TABLE 2. iso*Propenyl compounds*, $CH_2{:}CMeX$.

| Compound | $\nu_{C:C}$, cm.$^{-1}$ | $\nu_{C:C}$, $\varepsilon$ | $\delta_{CH_2}$, cm.$^{-1}$ | $\delta_{CH_2}$, $\varepsilon$ |
|---|---|---|---|---|
| *Esters* (X = O·CO·R) | | | | |
| Acetate | 1673 | 80 | 869 | 110 |
| | | | (899) | (60) |
| Benzoate | 1676 | ~70 | 877 | ~75 |
| Summary | 1674 ± 2 | ~80 | 873 ± 6 | ~100 |
| iso*Propenyl ketones* (X = CO·R) | | | | |
| Methyl | 1632 | 39 | 930 | 110 |
| 2-Chloroethyl | 1654 | — | 931 | ~50 |
| Summary | [d] | — | 930 ± 1 | 50—110 |
| *Conjugated diolefins* (X = CR:CR′R″) [e] | | | | |
| $CH_2{:}CMe{\cdot}CH{:}CHMe$ (API 452) | — | — | 883 | — |
| $CH_2{:}CMe{\cdot}CMe{:}CH_2$ (API 451) | — | — | 890 | — |
| $CH_2{:}CMe{\cdot}CH{:}CH_2$ (API 278) | — | — | ~895 | — |
| Summary | — | — | 889 ± 5 | — |
| *Miscellaneous* | | | | |
| X = $CO_2H$ | 1632 | ~100 | 947 | 100 |
| X = CN | 1620 | 22 | 929 | 110 |

TABLE 3. *Acrylates and methacrylates.*

| | $\nu_{C:O}$ | $\nu_{C:C}$ | $\delta_{CH}$ | A | B | C | D | $\delta_{CH}$ | $\delta_{CH}$ |
|---|---|---|---|---|---|---|---|---|---|
| *Acrylates* | | | | | | | | | |
| *cyclo*Hexyl | 1725 | 1640 | 1407 | 1298 | 1272 | 1192 | 1050 | 983 | 964 |
| | (120) | (40) | (100) | (130) | (150) | (140) | (115) | (100) | (100) |
| | | 1622 | | | | | | | |
| | | (42) | | | | | | | |
| 2-Ethyl- | 1723 | 1637 | 1407 | 1295 | 1270 | 1180 | 1054 | 983 | 964 |
| hexyl | (140) | (40) | (100) | (120) | (140) | (160) | (100) | (100) | (85) |
| | | 1625 | | | | | | | |
| | | (38) | | | | | | | |
| *iso*Propyl | 1717 | 1640 | 1407 | 1295 | 1274 | 1196 | 1047 | 984 | 965 |
| | (140) | (55) | (95) | (130) | (140) | (130) | (95) | (100) | (85) |
| | | 1619 | | | | 1182 | | | |
| | | (50) | | | | (120) | | | |
| Methyl | 1735 | 1637 | 1404 | 1290 | 1273 | 1197 | 1068 | 984 | 965 |
| | (140) | (45) | (90) | (90) | (150) | (150) | (110) | (105) | (80) |
| | | 1625 | | | | 1179 | | | |
| | | (35) | | | | (150) | | | |
| Ethyl | 1726 | 1637 | 1406 | 1285 | 1271 | 1187 | 1060 | 984 | 965 |
| | (120) | (38) | (110) | (130) | (150) | (160) | (110) | (95) | (75) |
| | | 1622 | | | | | | | |
| | | (30) | | | | | | | |
| Allyl | 1723 | 1635 | 1405 | 1296 | 1271 | 1184 | 1049 | 983 (i) | 966 |
| | (130) | (47) | (97) | (120) | (140) | (90) | (90) | (135) | (110) |
| | | 1620 | | | | | | | |
| | | (43) | | | | | | | |
| Summary | 1723 ± 4 [f] | 1638 ± 2 | 1406 ± 1 | 1293 ± 5 | 1272 ± 2 | 1187 ± 4 [e] | 1055 ± 8 | 984 ± 1 | 965 ± 1 |
| | (120—140) | (38—55) | (90—110) | (90—130) | (140—150) | (90—160) | (90—115) | (95—105) | 75—110 |
| | | 1622 ± 2 | | | | | | | |
| | | (30—50) | | | | | | | |
| *Methacrylates* | | | | | | | | | |
| *n*-Butyl | 1717 | 1640 | 1404 | 1318 | 1297 | 1156 | 1011 | — | 938 |
| | (140) | (65) | (47) | (140) | (140) | (160) | (50) | — | (120) |
| 2-Ethyl- | 1717 | 1635 | 1404 | 1321 | 1296 | 1163 | 1013 | — | 939 |
| hexyl | (130) | (67) | (52) | (130) | (140) | (160) | (70) | — | (120) |
| Allyl | 1714 | 1635 | 1404 | 1314 | 1295 | 1156 | 1012 | — | 939 |
| | (140) | (70) | (38) | (130) | (130) | (160) | (70) | — | (140) |
| Summary | 1716 ± 2 | 1637 ± 3 | 1404 | 1318 ± 5 | 1296 ± 1 | 1158 ± 4 | 1012 ± 1 | — | 939 ± 1 |
| | (130—140) | (65—70) | (38—52) | (130—140) | (130—140) | (160) | (50—70) | — | (120—140) |

*Note.*—Unbracketted figures are frequencies (cm.$^{-1}$), bracketted figures are absorptivities ($\varepsilon$).

in a 0·2-mm. cell) with a Grubb–Parsons single-beam spectrometer and rock-salt prism. Frequencies are within 3 cm.$^{-1}$ in the 1600-cm.$^{-1}$ region, and 1 cm.$^{-1}$ in the 900-cm.$^{-1}$ region.

Intensities are expressed as group molar absorptivities ($\varepsilon$) given by absorbance ($\log_{10} I_0/I$) divided by the product of optical path in cm. and concentration in g.-equiv./l.

The results are tabulated for vinyl (Table 1) and *iso*propenyl groups (Table 2). Acrylates and methacrylates (Table 3) are given separately and include absorptions not associated with the olefinic groups. Frequencies are summarised by the mean and standard deviation, and the correlations are given in Table 4. The 1400-cm.$^{-1}$ band was not investigated in many cases (marked N.I.).

TABLE 4. *Olefinic group correlations.*

| Group | No. of cpds. | $\nu_{C:C}$ | $\Delta\nu$ [h] | $\varepsilon$ | $\delta_{CH}$ | $\Delta\nu$ [h] | $\varepsilon$ | $\delta_{CH}$ | $\Delta\nu$ [h] | $\varepsilon$ |
|---|---|---|---|---|---|---|---|---|---|---|
| *Type* $CH_2$:CH. | | | | | | | | | | |
| $CH_2$:CHR [g] ..... | — | 1642 ± 3 | 0 | 28—44 | 997 ± 6 | 0 | 33—57 | 912 ± 4 | 0 | 110—150 |
| $CH_2$:CH·CR':CR'R'' | 5 | N.I. | — | — | 1000 ± 9 | + 3 | — | 904 ± 7 | − 8 | — |
| $CH_2$:CH·$CH_2$·OR ... | 4 | 1645 ± 2 | + 3 | 6—20 | 989 ± 1 | − 8 | 36—90 | 923 ± 2 | +11 | 85—100 |
| $CH_2$:CH·$CH_2$·O·CO·R | 4 | 1652 ± 3 | +10 | ~27 | 985 ± 3 | −12 | 90—100 | 932 | +20 | 90—100 |
| | | | | | | | | 922 ± 1 | +10 | 72—84 |
| $CH_2$:CH·OR ..... | 5 | 1634 ± 3 | − 8 | 65—74 | 962 ± 2 | −35 | 55—80 | 942 ± 1 | +30 | 28—40 |
| | | 1611 ± 4 | −31 | 110—120 | | | | | | |
| $CH_2$:CH·O·CO·R ..... | 3 | 1647 | + 5 | 90—120 | 948 ± 1 | −49 | 90—105 | 870 ± 2 | −42 | 110—130 |
| $CH_2$:CH·$CO_2$R ..... | 6 | 1638 ± 2 | − 4 | 38—55 | 984 ± 1 | −13 | 95—100 | 965 ± 1 | +53 | 75—100 |
| | | 1622 ± 2 | −20 | 30—50 | | | | | | |
| $CH_2$:CH·CO·R ..... | 3 | 1619 ± 1 | −23 | 48—90 | 983 ± 1 | −14 | 68—100 | 954 ± 1 | +42 | 65—120 |
| *Type* $CH_2$:CMe. | | | | | | | | | | |
| $CH_2$:CRR' [g] ..... | — | 1650 ± 11 | 0 | 20—42 | — | — | — | 889 ± 6 | 0 | 120—200 |
| $CH_2$:CMe·CR':CR'R'' | 3 | N.I. | — | — | — | — | — | 889 ± 5 | 0 | — |
| $CH_2$:CMe·O·CO·R ... | 2 | 1674 ± 2 | +24 | ~80 | — | — | — | 873 ± 6 | −16 | ~100 |
| $CH_2$:CMe·$CO_2$R ..... | 3 | 1637 ± 3 | −13 | 65—70 | — | — | — | 939 ± 1 | +50 | ~125 |
| $CH_2$:CMe·CO·R ..... | 2 | [d] | — | — | — | — | — | 930 ± 1 | +41 | 50—110 |

[g] Based on data of McMurray and Thornton, *loc. cit.*
[h] Frequency shift from unconjugated hydrocarbon value.

## DISCUSSION

All the characteristic absorptions for classes of polar-substituted vinyl and *iso*propenyl groups have standard deviations of within 4 cm.$^{-1}$, and this, together with the large shifts observed between the classes of compounds, indicates that the correlations are reliable, even when only a small number of compounds has been examined for a given class.

Even when purely empirical, such correlations are of value for identification and structural determinations, but an understanding of the reasons for the frequency shifts would greatly assist in extending the results to new compounds.

The effect most readily interpreted is that of conjugation which lowers $\nu_{C:C}$. In the diolefins the interpretation is complicated by the effects of mechanical coupling and the selection rules, and for this reason values of $\nu_{C:C}$ are omitted from the Tables. Butadiene, for example, has an infra-red band at 1592 cm.$^{-1}$, and a Raman shift at *ca.* 1653 cm.$^{-1}$, the result of coupling. The mean value of *ca.* 1614 is lower than normal, presumably owing to conjugation (Sheppard and Simpson, *loc. cit.*, p. 32).

Where coupling does not occur, the observed value of $\nu_{C:C}$ is approximately related to the strength of the bond. Thus conjugation accounts for the lowering of $\nu_{C:C}$ in conjugated nitriles ($\nu_{C\equiv N}$ is also lowered; Sheppard and Sutherland, *J.*, 1947, 453; Kitson and Griffith, *Analyt. Chem.*, 1952, **24**, 334) and in conjugated ketones and esters of α-unsaturated acids ($\nu_{C:O}$ is also lowered; Hartwell, Richards, and Thompson, *J.*, 1948, 1436). For the esters of unsaturated alcohols, however, $\nu_{C:C}$ is raised (as is $\nu_{C:O}$; *idem, ibid.*).

The doubling of $\nu_{C:C}$ for the vinyl ethers and the acrylates is probably due to rotational isomerism rather than Fermi degeneracy, but in the absence of low-temperature spectra of the crystals a decision cannot be made. It seems unlikely that such consistent splitting is due to degeneracy, since this would require a further characteristic absorption (below

650 cm.$^{-1}$) to give a second overtone or a combination degenerate with $\nu_{C:O}$. The doubling of $\nu_{C:O}$ in vinyl ketones also suggests rotational isomerism.

In consideration of the effect of polar groups upon the $\delta_{CH}$ absorptions at 850—1000 cm.$^{-1}$, conjugation is obviously unimportant (from the negligible shifts for the diolefins). Furthermore, an examination of the vinyl correlations shows that no single parameter can explain the shifts of the two bands. For example, in general the absorptions move in opposite directions, but for the vinyl esters both absorptions move to lower frequencies. However, the vinyl ester 870-cm.$^{-1}$ absorption may be wrongly assigned, and the two $\delta_{CH}$ absorptions may be superimposed at 948 cm.$^{-1}$ (cf. acrylonitrile, Table 1). There is a general qualitative parallelism between the shifts for vinyl and *iso*propenyl compounds similar to that reported for vinyl and vinylidene halides (Sheppard, Thesis, Cambridge, 1947, pp. 109 *et seq.*).

The large frequency shifts arising from polar substituents, and the constancy of the correlations, suggest that polar and electron-displacement effects, rather than mass effects, are responsible. In such a case, one might expect that the shifts would be algebraically additive when more than one substituent is present; unfortunately, only two suitable compounds were available to test this suggestion.

For 3 : 3-diethoxyprop-1-ene, $CH_2$:CH·$CH(OEt)_2$, the shifts may be regarded as twice those for an allyl ether, *viz.*, $997 - 2 \times 8 = 981$ (obs. 986 cm.$^{-1}$) and $912 + 2 \times 11 = 934$ (obs. 935 cm.$^{-1}$). 3-Acetoxy-3-cyanoprop-1-ene may be regarded as having the shifts of an allyl ester imposed upon the frequencies for allyl cyanide, *viz.*, $984 - 12 = 972$ (obs. 978 cm.$^{-1}$) and $928 + 20 = 948$ (obs. 946 cm.$^{-1}$); although the agreement is quite good, further reference compounds would be needed to test the suggested additivity.

The possible use of the 1400-cm.$^{-1}$ absorption was not realised until much of the experimental work was completed, and the results are therefore incomplete with respect to this band. The relatively small range of frequencies observed (1404—1425 cm.$^{-1}$) suggests that, although the band might be useful for confirming the presence of the olefinic group, it would be of little value for deciding the nature of the substitution.

In addition to the olefinic absorptions, acrylates and methacrylates (Table 3) have five strong characteristic absorptions; those designated C and D are probably associated with the C–O vibrations observed in other esters (Thompson and Torkington, *J.*, 1945, 640). The A and B bands may be $\delta_{CH}$ (in plane) modes (Sheppard and Simpson, *loc. cit.*, Tables 4 and 7).

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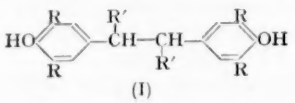
## 532. *Substitution Reactions of Hexœstrol and Analogous Compounds.*

By Ng. Ph. Buu-Hoï, Denise Lavit, and Ng. D. Xuong.

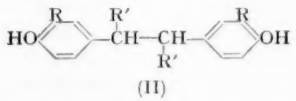
Halogenation of hexœstrol (*meso*-3 : 4-di-*p*-hydroxyphenylhexane) by sulphuryl chloride, bromine, or iodine, is shown to give predominantly the corresponding tetra-substituted derivatives, whereas nitration in acetic acid medium gives a dinitro-product. Similar results are recorded with higher homologues of hexœstrol, with 4 : 4′-dihydroxydibenzyl, and various 4 : 4′-dihydroxydiphenylmethanes. During this research, several *o*-aminophenols and benzoxazoles of the same series were prepared as potential tuberculostatic agents.

Hexœstrol (*meso*-3 : 4-di-*p*-hydroxyphenylhexane) is a readily available intermediate (cf. Buu-Hoï and Hoán, *J. Org. Chem.*, 1949, **14**, 1023) for the preparation of compounds built on the same molecular pattern as synthetic œstrogens, and with possible pituitary-inhibitory and antithyroid activity.

Halogenation reactions of hexœstrol have now been studied, as these should result in compounds bearing halogen atoms at 3 : 5-positions, as with tetrachloro- and tetrabromothyronine (Lerman and Harington, *J. Clin. Invest.*, 1948, **27**, 546; Richards, Brady, and Riggs, *J. Clin. Endocrinol.*, 1949, **9**, 1107) and other thyroxin analogues (cf. Wilkinson, Sheehan, and Maclagan, *Biochem. J.*, 1951, **48**, 188; **49**, 710, 714). Treatment of hexœstrol with sulphuryl chloride or bromine in excess readily gave 3 : 5 : 3′ : 5′-tetrachlorohexœstrol



(I)

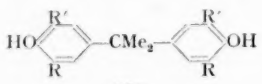


(II)

(I; R = Cl, R′ = Et) and 3 : 5 : 3′ : 5′-tetrabromohexœstrol (I; R = Br, R′ = Et). 3 : 5 : 3′ : 5′-Tetraiodohexœstrol (Oxley, Lowe, Peak, and Watkins, *J.*, 1951, 3288) was similarly obtained from iodine and yellow mercuric oxide. Homologues of hexœstrol reacted in the same way, 4 : 4′-dihydroxydibenzyl and *meso*-4 : 5-di-*p*-hydroxyphenyl-2 : 7-dimethyloctane giving the corresponding 3 : 5 : 3′ : 5′-tetrahalogenated derivatives.

Nitration of hexœstrol in acetic acid medium afforded 3 : 3′-dinitrohexœstrol (II; R = $NO_2$, R′ = Et), and the same reaction was observed with its homologues such as 4 : 4′-dihydroxydibenzyl, *meso*-4 : 5-di-*p*-hydroxyphenyloctane and *meso*-4 : 5-di-*p*-hydroxyphenyl-2 : 7-dimethyloctane.

Hexœstrol and its homologues thus closely resembled 4 : 4′-dihydroxydiphenylmethanes, both in respect of halogenation (cf. Zincke and Grueters, *Annalen*, 1905, **343**, 86; Zincke and Goldemann, *ibid.*, 1908, **362**, 205; Auwers and Rietz, *ibid.*, 1907, **356**, 154) and of nitration (cf. Széky, *Chem. Zentr.*, 1904, **11**, 1737). From 2 : 2-di-*p*-hydroxyphenylpropane, Széki obtained 2 : 2-di-(4-hydroxy-3-nitrophenyl)propane (III; R = $NO_2$,



(III)

(IV)

R′ = H), m. p. 133°, which was reduced by stannous chloride to a diamine of m. p. 218—219°; repetition of this experiment showed the m. p. of the dinitro-compound to be in accord with that of Széki's compound, but the diamine had m. p. 270°. Similar nitration of 2 : 2-di-(4-hydroxy-3-methylphenyl)propane (III; R = Me, R′ = H) yielded the dinitro-product (III; R = Me, R′ = $NO_2$). No proof has previously been provided for the position of nitration of 4 : 4′-dihydroxydiphenylmethane, apart from analogy with *p*-cresol. The orientation has now been established by conversion of the diamine (III; R = $NH_2$,

R′ = H) into 2 : 2-di-(2-methyl-5-benzoxazolyl)propane (IV; R = H) by acetic anhydride; a similar compound (IV; R = Me) was obtained from the reduction product of 2 : 2-di-(4-hydroxy-3-methyl-5-nitrophenyl)propane. In view of the significant tuberculostatic activity of *o*-aminophenol (Jouin and Buu-Hoï, *Ann. Inst. Pasteur*, **1946**, **72**, 580), the above amines are of interest as potential antitubercular agents, as also is 3 : 3′-diaminohexœstrol (II; R = $NH_2$, R′ = Et), prepared by reduction of the corresponding dinitro-compound. 3 : 5 : 3′ : 5′-Tetrabromohexœstrol, kindly tested by Mrs. Pitt-Rivers (at the National Institute for Medical Research, London), showed no antithyroxine action as assayed by the method of goitre prevention in rats; 3 : 3′-diaminohexœstrol dihydrochloride has shown marked tuberculostatic activity *in vitro*, as was expected.

## Experimental

3 : 5 : 3′ : 5′-*Tetrachlorohexœstrol* (I; R = Cl, R′ = Et).—To a solution of recrystallised hexœstrol (m. p. 187°; 2 g.) in anhydrous chloroform (200 c.c.), sulphuryl chloride (6 g.) was added in small portions with stirring; the mixture was refluxed for 6 hr., the chloroform distilled off, and the solid residue recrystallised from acetic acid, giving the *tetrachloro*-compound (2·5 g.) as prisms, m. p. 203° (Found: C, 53·0; H, 4·4. $C_{18}H_{18}O_2Cl_4$ requires C, 52·7; H, 4·4%). Use of less sulphuryl chloride (3 g.) resulted in the same product after repeated crystallisation, the more soluble portions consisting of chlorine-containing substances melting over a wide range and of some recovered hexœstrol. The *dimethyl ether*, prepared from 3 : 5 : 3′ : 5′-tetrachlorohexœstrol (0·5 g.), methyl iodide (0·4 g.), and potassium hydroxide (0·16 g.) in ethanol, formed needles, m. p. 183°, from ethanol (Found: C, 54·6; H, 5·2. $C_{20}H_{22}O_2Cl_4$ requires C, 54·8; H, 5·0%).

3 : 5 : 3′ : 5′-*Tetrabromohexœstrol*.—To a solution of hexœstrol (4 g.) in acetic acid (400 c.c.), bromine (9·5 g. in acetic acid) was added in small portions with stirring; after 2 hr., water was added, and the solid precipitate collected, washed with water, and recrystallised from acetic acid, giving the *tetrabromo*-compound as needles (5 g.), m. p. 230° (Found: C, 37·0; H, 3·2. $C_{18}H_{18}O_2Br_4$ requires C, 36·9; H, 3·1%); an attempt to obtain 3 : 3′-dibromohexœstrol by using less bromine (4 g.) failed. The *dimethyl ether*, prepared as above, formed, from ethanol–benzene, needles, m. p. 211° (Found: C, 39·0; H, 3·6. $C_{20}H_{22}O_2Br_4$ requires C, 39·1; H, 3·6%).

3 : 5 : 3′ : 5′-*Tetraiodohexœstrol*.—To a mixture of hexœstrol (4 g.), yellow mercuric oxide (13 g.), and ethanol (150 c.c.) was added pulverised iodine (15 g.) in small portions with shaking. After 1 hr., the solid was filtered off and washed with hot ethanol; the filtrate gave on dilution with water a precipitate, which was recrystallised first from acetic acid, then from ethanol, giving almost colourless prisms (5 g.), melting at 233°, solidifying again, then re-melting at 236°; Oxley *et al.* (*loc. cit.*) gave m. p. 239°. The *dimethyl ether* formed prisms, m. p. 206°, from ethanol–benzene (Found: C, 30·5; H, 2·9. $C_{20}H_{22}O_2I_4$ requires C, 29·9; H, 2·7%).

3 : 3′-*Dinitrohexœstrol* (II; R = $NO_2$, R′ = Et).—A fine suspension of hexœstrol (10 g.) in cold acetic acid (600 c.c.) was treated with nitric acid (*d* 1·33; 5·2 g. in acetic acid) in small portions with stirring; a clear solution was obtained, which soon deposited crystals of 3 : 3′-*dinitrohexœstrol*. After 1 hr. at room temperature, the precipitate was collected, washed with water, and recrystallised from acetic acid, giving pale yellow needles (10 g.), m. p. 233° (Found: C, 60·0; H, 5·7. $C_{18}H_{20}O_6N_2$ requires C, 60·0; H, 5·6%).

3 : 3′-*Diaminohexœstrol*.—A suspension of the foregoing compound (11 g.) in ethanol (500 c.c.) was treated with a solution of stannous chloride (50 g.) in hydrochloric acid (70 c.c.) in small portions with stirring, and the mixture refluxed for 6 hr. The ethanol was distilled off, the residue treated with dilute aqueous ammonia to pH 3, and the precipitate filtered off and washed with water. The filtrate was treated with more ammonia to pH 7, and the precipitated *amine* collected, washed with water, dried, and recrystallised from ethanol, giving grey-tinged prisms (5 g.), m. p. 273° (darkening above 260°), soluble in hydrochloric acid or aqueous sodium hydroxide (Found: C, 71·6; H, 8·2; N, 9·0. $C_{18}H_{24}O_2N_2$ requires C, 72·0; H, 8·0; N, 9·3%).

meso-4 : 5-*Di*-(3 : 5-*dibromo*-4-*hydroxyphenyl*)-2 : 7-*dimethyloctane* (I; R = Br; R′ = $Bu^i$).—A solution of *meso*-4 : 5-di-(4-hydroxyphenyl)-2 : 7-dimethyloctane (4 g.; m. p. 207°), prepared according to Buu-Hoï and Hoán (*loc. cit.*), in acetic acid (400 c.c.) was treated with bromine (7·8 g.) in the usual way, giving a *product* which formed needles (5 g.), m. p. 210°, from acetic acid (Found: C, 41·3; H, 4·0. $C_{22}H_{26}O_2Br_4$ requires C, 41·1; H, 4·1%). The *dimethyl ether* crystallised from ethanol as prisms, m. p. 178° (Found: C, 43·4; H, 4·7. $C_{24}H_{30}O_2Br_4$ requires C, 43·0; H, 4·5%).

meso-4 : 5-*Di*-(4-*hydroxy*-3-*nitrophenyl*)*octane* (II; R = $NO_2$, R′ = $Pr^n$).—A solution of *meso*-4 : 5-di-*p*-hydroxyphenyloctane (2·5 g.; m. p. 168—169°) in acetic acid, treated with nitric acid (1·2 g.), yielded a compound (1·8 g.) crystallising from acetic acid as yellow prisms, m. p. 218° (Found : C, 61·8; H, 6·2. $C_{20}H_{24}O_6N_2$ requires C, 61·8; H, 6·2%).

meso-4 : 5-*Di*-(4-*hydroxy*-3-*nitrophenyl*)-2 : 7-*dimethyloctane* (II; R = $NO_2$, R′ = $Bu^i$).—From acetic acid this *phenol* formed yellow needles, m. p. 182° (Found : C, 63·3; H, 6·7. $C_{22}H_{28}O_6N_2$ requires C, 63·5; H, 6·7%).

3 : 5 : 3′ : 5′-*Tetrabromo*-4 : 4′-*dihydroxydibenzyl* (I; R = Br, R′ = H).—4 : 4′-Dihydroxydibenzyl was prepared from 4-methoxybenzyl chloride by treatment with iron powder in aqueous medium (cf. Buu-Hoï and Hoán, *loc. cit.*), and demethylation of the resulting 4 : 4′-dimethoxydibenzyl with pyridine hydrochloride. A solution of 4 : 4′-dihydroxydibenzyl (4 g.) in acetic acid (300 c.c.) was treated with bromine (12 g. in acetic acid) in the usual way; the *product* (5·5 g.) crystallised as prisms, m. p. 195°, from acetic acid (Found : C, 31·6; H, 2·2. $C_{14}H_{10}O_2Br_4$ requires C, 31·7; H, 1·9%). The *dimethyl ether* formed needles, m. p. 191°, from ethanol (Found : C, 34·2; H, 2·6. $C_{16}H_{14}O_2Br_4$ requires C, 34·4; H, 2·5%).

4 : 4′-*Dihydroxy*-3 : 5 : 3′ : 5′-*tetraiododibenzyl* (I; R = I, R′ = H).—Prepared by Oxley's procedure (Oxley *et al.*, *loc. cit.*), this formed fine colourless prisms, m. p. 237°, from acetic acid (Found : I, 70·4. $C_{14}H_{10}O_2I_4$ requires I, 70·8%). The *dimethyl ether* formed needles, m. p. 215°, from ethanol (Found : C, 25·4; H, 2·0. $C_{16}H_{14}O_2I_4$ requires C, 25·7; H, 1·9%).

4 : 4′-*Dihydroxy*-3 : 3′-*dinitrodibenzyl* (II; R = $NO_2$, R′ = H).—An ice-cooled solution of 4 : 4′-dihydroxydibenzyl (3 g.) in acetic acid (300 c.c.) was treated with nitric acid in the usual way; the product crystallised as pale yellow needles, m. p. 198°, from acetic acid (Found : C, 55·0; H, 4·0. $C_{14}H_{12}O_6N_2$ requires C, 55·3; H, 3·9%).

2 : 2-*Di*-(3-*amino*-4-*hydroxyphenyl*)*propane*.—2 : 2-Di-(4-hydroxy-3-nitrophenyl)propane (11 g.; m. p. 134°) was reduced by stannous chloride (45 g. in 70 c.c. of hydrochloric acid) as for 3 : 3′-diaminohexœstrol; the diamine (8·5 g.) formed fine, grey-tinged needles, m. p. 271° (darkening above 256°), from ethanol, with amphoteric properties (Found : C, 69·7; H, 7·1; N, 10·8. Calc. for $C_{15}H_{18}O_2N_2$ : C, 69·8; H, 7·0; N, 10·9%); Széki gave m. p. 218—219°.

2 : 2-*Di*-(2-*methyl*-5-*benzoxazolyl*)*propane* (IV; R = H).—A mixture of the foregoing diamine (1 g.) and acetic anhydride (5 g.) was refluxed for 3 hr., and the product vacuum-distilled; recrystallisation gave prisms (0·5 g.), m. p. 72°, from light petroleum (Found : C, 74·0; H, 5·9. $C_{19}H_{18}O_2N_2$ requires C, 74·5; H, 5·9%).

2 : 2-*Di*-(4-*hydroxy*-3-*methyl*-5-*nitrophenyl*)*propane*.—A suspension of the condensation product (20 g.) of acetone with *o*-cresol in acetic acid, when treated with nitric acid (11 g.) in the usual way, gave a single *product*, crystallising as yellow needles (9 g.), m. p. 195°, from acetic acid (Found : C, 58·8; H, 5·2. $C_{17}H_{18}O_6N_2$ requires C, 59·0; H, 5·2%).

2 : 2-*Di*-(2 : 4-*dimethyl*-5-*benzoxazolyl*)*propane* (IV; R = Me).—Reduction of the foregoing dinitro-compound (8·5 g.) with stannous chloride (40 g.) gave a diamine (5 g.) which was heated for 3 hr. with acetic anhydride; after vacuum-distillation, the *product* formed prisms, m. p. 127°, from methanol (Found : C, 75·3; H, 6·5. $C_{21}H_{22}O_2N_2$ requires C, 75·4; H, 6·6%).

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# 533. *A Quantum-mechanical Treatment of Aliphatic Compounds. Part I. Paraffins.*

By R. D. Brown.

A new general quantum-mechanical treatment of molecular structure is described, applicable to all types of molecules, and especially to aliphatic compounds. It consists of a molecular-orbital treatment in which the orbitals are represented as linear combinations of united-atom orbitals, located in every bond in the molecule. The various parameters which arise in the theory are discussed; they are analogous to the parameters occurring in the LCAO molecular-orbital treatment of conjugated systems.

A convenient expansion for the total electronic energy of a molecule is obtained in powers of $S$, the overlap integral between orbitals in adjacent C–H bonds. The results are compared with experimental heats of formation of the paraffins and, by extension of the calculations to alkyl radicals, with various bond-dissociation energies. The agreement between theory and experiment is satisfactory.

It is shown that the electron densities in the various bonds are equal. This makes the theoretical treatment " self-consistent " and means that chemical reactivities must be discussed in terms of polarizabilities or activation energies rather than in terms of the charge distribution.

The application of quantum-mechanical approximations to problems of molecular structure and reactivity has been extensively developed in recent years for conjugated and aromatic compounds because it has been possible to focus attention solely on the $\pi$-electrons, any effects arising from the $\sigma$-electrons being regarded as unimportant or constant. Particularly in the case of the molecular-orbital approximation, a general theory of conjugated systems has been formulated (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; **192**, 16; 1948, *A*, **193**, 447; **195**, 188; Chirgwin and Coulson, *ibid.*, 1950, *A*, **201**, 196) and has had considerable success as a basis of theories of chemical reactivity (Brown, *Quart. Reviews*, 1952, **6**, 63). However no analogous general treatment has hitherto been published for saturated molecules. Such molecules are treated in the present paper.*

The approximations employed for conjugated systems, namely, the valence-bond and LCAO molecular-orbital approximations, ultimately stem from approximations developed for the treatment of simple diatomic molecules (Heitler and London, *Z. Physik*, 1927, **44**, 455; Hund, *ibid.*, 1928, **51**, 759; Mulliken, *Phys. Review*, 1928, **32**, 186, 761; Lennard-Jones, *Trans. Faraday Soc.*, 1929, **25**, 668) and have the common feature that the wave functions are built up from atomic orbitals centred on each atom in the system. This results in considerable complexity for larger molecules when the atomic interactions are in tetrahedral directions, although not for the simpler planar $\pi$-type interactions, and so it is not surprising that the theory has developed more rapidly for the latter systems. This defect has been overcome in the present method by rejecting atomic-centred orbitals as the basis of the molecular wave-functions. Instead, the basis is taken to be a set of orbitals situated in each bond of the molecule, so that in methane, for example, the eight $\sigma$-electrons are considered to move in molecular orbitals formed by appropriate linear combinations of more localized $\sigma$-orbitals situated in each of the C–H bonds. In the case of diatomic molecules these bond orbitals are simply the united-atom orbitals which would accommodate the molecular electrons if the nuclei could be united; indeed, the present approach was stimulated by a recent revival of interest in the united-atom viewpoint of molecular binding (Matsen, in the press; Brown and Matsen, in the press).

The molecular orbitals for the $\sigma$-electrons will therefore be written :

$$\psi_j = \sum_{r=1}^{N} c_{jr}\,\phi_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* A similar treatment has also been investigated by Professor C. A. Coulson (personal communication).

where $\phi_r$ is a united-atom σ-orbital located in the $r$th bond of the molecule, the summation in (1) being taken over all $N$ bonds in the molecule. The coefficients for the molecular orbitals, $c_{rj}$, may be determined by the variation method (*e.g.*, Kemble, " Fundamental Principles of Quantum Mechanics," McGraw-Hill, New York, 1937, p. 408), and lead to the familiar secular equations :

$$\sum_{r=1}^{N} c_{jr}\,(H_{jr} - eS_{jr}) = 0,\ j = 1 \ldots N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the $N$ roots of which, $e_j$, correspond to the energies of the molecular orbitals. To solve expression (2) we require values for the matrix elements :

$$H_{jr} = \int \phi_j \mathscr{H} \phi_r \, d\tau ;\ S_{jr} = \int \phi_j \phi_r d\tau$$

which are analogous to the matrix elements in the molecular-orbital treatment of conjugated systems. The following analogous assumptions will be made. The coulomb integral, $H_{mm}$, of an orbital, $\phi_m$, depends only on the type of bond in which it resides; thus all C–H bond orbitals will be assumed to have a coulomb integral $\alpha$. The resonance integral, $H_{mn}$, between orbitals $\phi_m$ and $\phi_n$ will be assumed to be zero, unless $m$ and $n$ are adjacent bonds in which case it will be taken to depend only on the type of bonds $m$ and $n$. When $m$ and $n$ are both C–H bonds the resonance integral will be taken to be β, and the resonance integrals for other pairs of bond orbitals will be assumed to have the values listed in Table 1. A similar set of values will be adopted for the overlap integrals, $S_{mn}$ (see Table 1).

TABLE 1. *Fundamental bond and interaction parameters.*

| Coulomb parameters | | Resonance parameters | | Overlap integrals | |
|---|---|---|---|---|---|
| Bond | Assumed val. | Bonds | Assumed val. | Bonds | Assumed val. |
| C–H | $\alpha$ | C–H ; C–H | $\beta$ | C–H ; C–H | $S$ |
| C–C | $\alpha + h\gamma$ | C–H ; C–C | $\theta\beta$ | C–H ; C–C | $\theta S$ |
| | | C–C ; C–C | $\eta\beta$ | C–C ; C–C | $\eta S$ |

The proportionality of resonance and overlap integrals has been assumed in order that the secular determinants may be simplified by means of manipulations due to Wheland (*J. Amer. Chem. Soc.*, **1942**, **64**, 900) in which energies are expressed in terms of the parameter $\gamma = \beta - S\alpha$, and the coulomb integrals of orbitals associated with bonds other than C–H are expressed in terms of $\alpha$ and $\gamma$ (see Table 1).

The above assumptions, all of which correspond to assumptions made in the MO treatment of conjugated systems, are more satisfactory in the present instance. Thus it is recognized (Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A*, **158**, 280; Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41; Coulson and Altmann, *Trans. Faraday Soc.*, 1952, **48** 293) that the resonance integral between a given pair of orbitals will vary with their distance apart; but bond lengths in unsaturated systems are known to vary considerably, while in saturated molecules very little relative variation is found experimentally, so that the actual variation in, say, β(C–H:C–H) will be much less than, say, the variation of β(C–C) in conjugated systems. It is also considered that the coulomb integral of a given kind of orbital will depend strongly on the electron density at that point in the molecule, and " self-consistent " procedures have been devised (Wheland and Mann, *J. Chem. Phys.*, 1949, **17**, 264; Laforgue, *J. Chim. phys.*, 1949, **46**, 568) to allow for this in those cases where the molecular charge distribution is not uniform. In the present treatment of saturated systems however it may be shown (see Appendix) that the electron distribution is uniform for all kinds of systems (not just for hydrocarbons), and so a treatment based on the above assumptions will always be " self-consistent."

If the values listed in Table 1 are inserted into the secular equations (2) it is a straightforward calculation to obtain the orbital energies, $e_j$, and hence the total electronic energy :

$$E = \sum_{j=1}^{N} 2e_j \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is convenient to expand $E$ in powers of $S$. It is then possible to obtain the first few terms of the expansion quite simply, as described in the Appendix, the simplification

arising mainly because in the case of saturated systems all the molecular orbitals are doubly filled with σ-electrons. The results for the first few paraffins are collected in Table 2.

TABLE 2. *Electronic energies of the paraffins.*

| Paraffin | $E$ | $H_f$ (kcal.) * |
|---|---|---|
| Methane | $8\alpha - 24S\gamma$ | −17·9 |
| Ethane | $14\alpha + 2h\gamma - (24 + 24\theta^2)S\gamma$ | −20·2 |
| Propane | $20\alpha + 4h\gamma - (28 + 40\theta^2 + 4\eta^2)S\gamma$ | −24·8 |
| Butane | $26\alpha + 6h\gamma - (32 + 56\theta^2 + 8\eta^2)S\gamma$ | −29·8 |
| *iso*Butane | $26\alpha + 6h\gamma - (36 + 48\theta^2 + 12\eta^2)S\gamma$ | −31·5 |
| Pentane | $32\alpha + 8h\gamma - (36 + 72\theta^2 + 12\eta^2)S\gamma$ | −35·0 |
| *iso*Pentane | $32\alpha + 8h\gamma - (40 + 64\theta^2 + 16\eta^2)S\gamma$ | −36·9 |
| *neo*Pentane | $32\alpha + 8h\gamma - (48 + 48\theta^2 + 24\eta^2)S\gamma$ | −39·7 |
| Hexane | $38\alpha + 10h\gamma - (40 + 88\theta^2 + 16\eta^2)S\gamma$ | −40·0 |
| 2-Methylpentane | $38\alpha + 10h\gamma - (44 + 80\theta^2 + 20\eta^2)S\gamma$ | −41·7 |
| 3-Methylpentane | $38\alpha + 10h\gamma - (44 + 80\theta^2 + 20\eta^2)S\gamma$ | −41·0 |
| 2 : 3-Dimethylbutane | $38\alpha + 10h\gamma - (48 + 72\theta^2 + 24\eta^2)S\gamma$ | −42·5 |
| 2 : 2-Dimethylbutane | $38\alpha + 10h\gamma - (52 + 64\theta^2 + 28\eta^2)S\gamma$ | −44·4 |

* Heat of formation at 25° (Rossini *et al.*, "Selected Values of Properties of Hydrocarbons" (circular c-461, Nat. Bur. Stand., Washington, 1947).

Some interesting deductions may be made from the results in Table 2, independent of the six * parameters in terms of which the energies are expressed. The most significant result is that to the first approximation ($S = 0$) *the total energy is the sum of the individual bond energies.* In the present case the energy of an isolated bond is equal to its coulomb term multiplied by the number of electrons present (*i.e.*, 2), so the C–H energy is $2\alpha$, and the C–C energy is $2\alpha + 2h\gamma$. The same general result can be established for all types of compound, not just for hydrocarbons (see Appendix). It is important that in the present treatment all the electrons are assigned to molecular orbitals embracing the whole molecule and possessing a wide range of orbital energies. The simple additivity property, more characteristic of a localized orbital treatment, arises "accidentally" because all orbitals happen to be fully occupied.

TABLE 3.

| Isomeric pair | $\delta E$ (kcal.) * | Isomeric pair | $\delta E$ (kcal.) * |
|---|---|---|---|
| Butane : *iso*butane | −1·7 | Hexane : 3-methylpentane | −1·0 |
| Pentane : *iso*pentane | −1·9 | Hexane : 2 : 3-dimethylbutane | $2 \times 1{\cdot}3$ † |
| Hexane : *iso*hexane | −1·7 | | |

* Differences in heats of formation at 25°.
† The corresponding theoretical difference is $2(\Gamma - \Phi)$.

When the energies are calculated to the second approximation (*i.e.*, with terms to the first power of $S$) the strict additivity no longer holds, and certain differences in energy are predicted for isomers. Thus the pairs of isomers, *n*-pentane–2 : 2-dimethylpropane and *n*-hexane–2 : 2-dimethylbutane, are predicted to have the same difference in electronic energies, namely $-(12 - 24\theta^2 + 12\tau_i^2)S\gamma$, which is conveniently written (cf. Table 5) $3(\Gamma - \Phi)$. Furthermore the pairs of isomers listed in Table 3 are predicted to have a constant energy difference of $\Gamma - \Phi$, *i.e.*, one-third of the preceding difference. We may test these predictions by using the experimental heats of formation of the hydrocarbons for their electronic energies † (see Table 2). The differences corresponding to $3(\Gamma - \Phi)$ are, respectively, −4·7 and −4·4 kcal., showing acceptable agreement between theory and experiment, and from these values we may predict that the differences $\Gamma - \Phi$ will be about −1·5 kcal. The experimental differences are listed in Table 3, and are gratifyingly near this figure, with a mean value of −1·5 kcal.

The present theory may be extended to deal with alkyl radicals. The simplest procedure, and the only one to be considered in detail here, is to suppose that the orbitals in the (planar) bonds around the carbon atom carrying the odd electron have the same

* Six parameters occur also in the analogous LCAO treatment of the energies of conjugated systems containing one heteroatom or monoatomic substituent.

† Since we are considering isomers, differences are also the differences in intrinsic energies, but the comparison with theory is not entirely satisfactory since the experimental data will include vibrational and rotational energy contributions. However similar comparisons have frequently been made for conjugated and aromatic compounds.

coulomb and resonance parameters as the corresponding orbitals for tetrahedral bonds, and to assign the odd electron to the customary $2p\pi$-orbital on this atom. The resonance integrals between this $\pi$-orbital and the adjacent $\sigma$-bond orbitals vanish in virtue of the antisymmetry of the $\pi$-orbital, and the $\sigma$-electrons can again be assigned to fill completely the molecular orbitals formed from the $\sigma$-bond orbitals, so that the convenient method of calculating total electronic energies, as described in the Appendix, is again applicable. A more refined procedure would be to introduce parameters for the orbitals in the bonds around the $sp^2$-carbon atom, differing from those of the corresponding tetrahedral orbitals, but this has the disadvantage of increasing the number of parameters appearing in the results, and so will not be considered here.

The energies to the second order for various paraffin radicals are given in Table 4.

TABLE 4. *Hydrocarbon radicals and* R–H *dissociation energies.*

| Radical | $E$ | $D$(R–H) Theor. | Exp.* |
|---|---|---|---|
| Methyl | $6\alpha - 12S\gamma$ | $F + 3\Phi$ 101·4 | 102 |
| Ethyl | $12\alpha + 2h\gamma - (16 + 20\theta^2)S\gamma$ | $F + 2\Phi$ 97·7 | 97 |
| *n*-Propyl | $18\alpha + 4h\gamma - (24 + 32\theta^2 + 4\Phi^2)S\gamma$ | $F + 2\Phi$ 97·7 | — |
| *iso*Propyl | $18\alpha + 4h\gamma - (24 + 32\theta^2 + 4\eta^2)S\gamma$ | $F + \Phi$ 94·0 | 94 |
| *n*-Butyl | $24\alpha + 6h\gamma - (24 + 52\theta^2 + 8\eta^2)S\gamma$ | $F + 2\Phi$ 97·7 | — |
| *iso*Butyl | $24\alpha + 6h\gamma - (28 + 44\theta^2 + 12\eta^2)S\gamma$ | $F + 2\Phi$ 97·7 | — |
| *sec.*-Butyl | $24\alpha + 6h\gamma - (28 + 48\theta^2 + 8\eta^2)S\gamma$ | $F + \Phi$ 94·0 | — |
| *tert.*-Butyl | $24\alpha + 6h\gamma - (36 + 36\theta^2 + 12\eta^2)S\gamma$ | $F$ 90·3 | 90 |

* Stevenson, *Discuss. Faraday Soc.*, 1951, **10**, 35, 113; Trotman-Dickenson, *ibid.*, p. 112.

Theoretical values for various dissociation energies, $D$(R–H), may be obtained by subtraction of the relevant hydrocarbon energies from Table 2, and these are also included in Table 4. They are conveniently expressed in terms of the parameters $F$ and $\Phi$, which are defined in Table 5. Table 5 also lists two other parameters, $G$ and $\Gamma$, and all the theoretical results discussed in the present paper depend only upon these four parameters. They are discussed further below (p. 2619).

TABLE 5. *Derived energy parameters.*

| Parameter | Definition | Assumed val. (kcal.) | Parameter | Definition | Assumed val. (kcal.) |
|---|---|---|---|---|---|
| $F$ | $-2\alpha + 12\theta^2 S\gamma$ | 90·3 | $\Phi$ | $4(1 - \theta^2)S\gamma$ | 3·7 |
| $G$ | $-2\alpha - 2h\gamma + 24\eta^2 S\gamma$ | 71·7 | $\Gamma$ | $4(\theta^2 - \eta^2)S\gamma$ | 2·1$_3$ |

It will be observed that the present theory (to the second order) groups R–H dissociation energies into four classes (methane-type, primary, secondary, tertiary), and predicts, independently of the values of any parameters, a uniform variation in the values from class to class. The uniform variation is confirmed experimentally by Stevenson's data for methane, ethane, propane, and *iso*butane (see Table 4), while the constancy of various primary $D$(R–H) and of various secondary $D$(R–H) has been remarked, *e.g.*, by Trotman-Dickenson (*Discuss. Faraday Soc.*, 1951, **10**, 112).

The theoretical dissociation energies, $D$(R–R′), for various C–C bonds are similarly derived from the data of Tables 2 and 4. They are conveniently expressed in terms of the parameters $G$ and $\Gamma$ of Table 5, *e.g.*, $D(C_2H_5\text{–}C_2H_5) = G + 4\Gamma$. Experimental dissociation energies may be derived from heats of formation of paraffin radicals (cf., *e.g.*, Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339; Szwarc, *Chem. Reviews*, 1950, **47**, 75), and comparison with theory may be made by using the assumed values of $G$ and $\Gamma$ listed in Table 5. For this purpose we have preferred to recalculate the heats of formation of paraffin radicals using Stevenson's more recent data (*loc. cit.*), and thence $D$(R–R′) for various bonds, rather than to employ the earlier tabulations of Roberts and Skinner or of Szwarc (*locc. cit.*). The latter are based on dissociation energies obtained from pyrolysis studies, and the data for *tert.*-butyl, and to some extent for *iso*propyl, are unreliable (see, *e.g.*, discussion by Szwarc, *loc. cit.*). The theoretical dissociation energies are compared with the experimental values (in parentheses) in Table 6. The two sets of figures agree extremely well, discrepancies being appreciably less than the uncertainty in the experimental figures, with the exception of $D$(R–R′) for 2 : 2 : 3 : 3-tetramethylbutane

($R = R' = Bu^t$). The experimental value in this case is about 5 kcal. less than the theoretical figure, and a plausible explanation immediately suggests itself. The theoretical treatment is based solely on the connectivity of all neighbouring bonds, and so does not include energy terms arising from the interactions of orbitals in different portions of the molecule which happen to approach one another because of the geometry of the molecule,

TABLE 6. *Dissociation energies of* C–C *bonds.**

| R | R′: Methyl | Ethyl | *iso*Propyl | *tert.*-Butyl |
|---|---|---|---|---|
| Methyl | 84·5 (84·$_4$) | 82·4 (81·$_7$) | 80·2 (80·$_8$) | 78·1 (78·$_3$) |
| Ethyl | — | 80·2 (79·$_4$) | 78·1 (78·$_9$) | 76·0 (75·$_7$) |
| *iso*Propyl | — | — | 76·0 (76·$_9$) | 73·8 (72·$_7$) |
| *tert.*-Butyl | — | — | — | 71·7 (67·$_6$) |

* Dissociation energies derived from heats of formation of alkyl radicals are given in parentheses.

*i.e.*, steric compressions of the van der Waals type. Such steric interactions will be greatest in the molecule under consideration, where the C–C bond concerned carries three methyl groups at each end. It is tempting to conclude from the present analysis that the compressional energy arising from the mutual repulsions of the six methyl groups amounts to about 5 kcal. The dissociation energy $D$ ($Pr^i$–$Bu^t$) is also slightly lower than predicted, although in this case the two values agree within the experimental uncertainty.

The treatment just discussed for alkyl radicals is equally applicable to the corresponding carbonium ions and carbanions, since the odd electron of the radical residues in a different "shell" from the σ-electrons, as discussed above. However, the resultant charge on the $sp^2$-carbon atom in these ions will doubtless affect the σ-bond orbitals immediately surrounding this carbon atom, just as in the simple LCAO treatment of conjugated systems a heteroatom is considered to affect the coulomb integrals of adjacent atoms. It is hoped to discuss these paraffin ions in terms of the present theory in a subsequent communication.

The preceding discussion of electronic energies is not complete without some further remarks concerning the parameters $F$, $G$, $\Phi$, $\Gamma$. These four parameters have been used to interpret a considerable number of independent experimental measurements of dissociation energies and heat-content differences, and the values assigned to them in Table 5 have been chosen to give the best fit with experiment. The parameter $G$ arises in the treatment of C–C dissociation energies, and its value simply determines the origin of the energy scale for these dissociation energies. The parameter $F$ plays an analogous part in the treatment of C–H dissociation energies. Clearly the selection of values of $F$ and $G$ to fit the observational data will help to eliminate any systematic error in the calculation of electronic energies of radicals in the present theory, *e.g.*, errors such as might arise from neglect of π–σ interactions.

The differences in the dissociation energies and in heats of formation are obtained solely in terms of $\Phi$ and $\Gamma$, so only two parameters are involved if we restrict considerations to differences rather than absolute values. It should perhaps be pointed out that the present treatment provides an acceptable prediction of energy differences of three essentially distinct types in terms of only two parameters.

It has already been mentioned that the first-order theory constitutes a theoretical justification for the additivity of bond energies. The second-order terms in the theory may also be interpreted quite simply. They arise from interactions of adjacent bonds. It can can be established generally (see Appendix) that the total energy to the second order consists of a sum of bond-energy terms and interaction-energy terms for adjacent bonds; the parameters $S\gamma$, $\theta^2 S\gamma$ and $\eta^2 S\gamma$ representing interactions of C–H with C–H, C–H with C–C, and C–C with C–C, respectively. The third-order terms (coefficient of $S^2$) which contain terms corresponding to mutual interactions of three adjacent bonds, include

additional terms which are no so simply interpreted. The present theory thus constitutes a theoretical justification for the empirical analysis of heats of formation of the paraffins by Platt (*J. Phys. Chem.*, 1952, **56**, 328), who included corrections to the simple additivity rule in terms of a parameter, $f$, representing the number of adjacent pairs of C–C bonds. The present analysis suggests that smaller corrections might be expressed in terms of mutual interactions of three adjacent bonds, rather than pairs of next-but-nearest neighbours, as was considered by Platt.

The present theory of saturated systems may be used to deal with the problem of chemical reactivities. It is natural, by analogy with the theory of conjugated systems, to suppose that the reactivity of a bond in heterolytic reactions might be correlated with the " bond charge density," which is defined by

$$Q_r = 2\sum_{j=1}^{N} c_{rj}^2 \quad (S = 0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for orthogonal orbitals, with a suitably modified definition for non-zero $S$ (see Appendix). However, it can be shown (Appendix) that all bonds have $Q_r = 2$, independently of $S$, *i.e.*, the σ-electron distribution over the bonds is uniform. Consequently the most promising approach to the problem of chemical reactivities appears to be by calculation of energies of activation. This application of the theory will be discussed in later papers.

## Appendix

In order to solve the secular equations (2), with the values of the matrix elements as set out in the preceding discussion, it is expedient to use the substitution (cf. Wheland, *loc. cit.*) :

$$(\alpha - e)/(\beta - S\alpha) = x/(1 - Sx) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The secular determinant then involves the numerical parameters $h$, $\theta$, and $\eta$ of Table 1, and the energy parameter, $x$, appears only in the leading diagonal. As an example, the resulting determinant for ethane is shown ($\delta = 1 - Sh$).

| | | | | | | |
|---|---|---|---|---|---|---|
| $x$ | 1 | 1 | $\theta$ | — | — | — |
| 1 | $x$ | 1 | $\theta$ | — | — | — |
| 1 | 1 | $x$ | $\theta$ | — | — | — |
| $\theta$ | $\theta$ | $\theta$ | $(\theta x + h)$ | $\theta$ | $\theta$ | $\theta$ |
| — | — | — | $\theta$ | $x$ | 1 | 1 |
| — | — | — | $\theta$ | 1 | $x$ | 1 |
| — | — | — | $\theta$ | 1 | 1 | $x$ |

The $N \times N$ determinant reduces to an $N$th degree polynomial in $x$, the zeros of which, $x_j$, correspond to the energies of the molecular orbitals :

$$e_j = \alpha - \frac{x_j}{1 - Sx_j}\gamma = \alpha - y_j\gamma, \text{ say, } . \quad (6)$$

and the total electronic energy is :

$$E = 2N\alpha - 2\gamma\sum_{j=1}^{N} y_j \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

To obtain explicit values for a particular $x_j$ (and so $y_j$) it is in general necessary to assign specific numerical values to $h$, $\theta$, and $\eta$, but it is possible to obtain $\sum_{j=1}^{N} y_j$ explicitly in terms of $h$, $\theta$, and $\eta$, as a power series in $S$, by employing some well-known formulæ of the theory of equations (see, *e.g.*, Turnbull, " Theory of Equations," Oliver and Boyd, Edinburgh, 1946). Thus if the polynomial in $x$ is

$$a_0x^N + a_1x^{N-1} + a_2x^{N-2} + \ldots\ldots$$

then we have :

$$\Sigma y_j = \Sigma x_j + S\Sigma x_j^2 + S^2\Sigma x_j^3 + \ldots\ldots$$

$$= \frac{-a_1}{a_0} + \frac{a_1^2 - 2a_0a_2}{a_0^2}S - \frac{a_1^3 - 3a_0a_1a_2 + 3a_0^2a_3}{a_0^3}S^2 + \quad . \quad . \quad . \quad (8)$$

and it remains to determine the coefficients, $a_n$.

Specific formulæ for the coefficients up to $a_6$ have been given by Coulson (*Proc. Camb. Phil. Soc.*, 1949, **46**, 202) for the particular case when $h = 0$, and $\theta = \eta = 1$. The formulæ we require may be obtained by an extension of his analysis. The main difference in the present case arises from terms involving powers of $h$ from the diagonal elements of the secular determinant. The coefficients $a_0$ and $a_1$ arise from only one term in the expansion of the determinant, namely, the product of the leading diagonal elements. These clearly comprise an element $(\delta x + h)$ for each C–C bond, and an element $x$ for each C–H bond. The paraffin

$C_nH_{2n+2}$ contains $(n - 1)$ C–C bonds and $(2n + 2)$ C–H bonds, and the coefficients $a_0$ and $a_1$ are, respectively :

$$a_0 = \delta^{n-1};\ a_1 = (n - 1)\delta^{n-2}h$$

Subsequent coefficients $a_2$, $a_3$, . . ., $a_N$, contain contributions from other terms of the secular determinant, and we find :

$$a_2 = \frac{(n-1)(n-2)}{2}\delta^{n-3}h^2 - (b_1\delta^{n-1} + b_2\theta^2\delta^{n-2} + b_3\gamma_i^2\delta^{n-3})$$

$$a_3 = \frac{(n-1)(n-2)(n-3)}{6}\delta^{n-4}h^3 - (b_1'\delta^{n-2} + b_2'\theta^2\delta^{n-3} + b_3'\gamma_i^2\delta^{n-4})h + 2(c_1\delta^{n-1} + c_2\theta^2\delta^{n-2} + c_3\gamma_i\theta^2\delta^{n-3} + c_4\gamma_i^3\delta^{n-4})$$

where $b$ and $c$ are the numbers of adjacent pairs or trios of bonds as follows : $b_1$, C–H ; C–H, *i.e.*, $C<^{H}_{H}$ ; $b_2$, C–H ; C–C, *i.e.*, $C<^{C}_{H}$ ; $b_3$, C–C ; C–C, *i.e.*, $C<^{C}_{C}$ ; $c_1$, C–H ; C–H, *i.e.*, $H-C<^{H}_{H}$ ; $c_2$, C–H; C–H; C–C, *i.e.*, $C-C<^{H}_{H}$ ; $c_3$, C–H; C–C; C–C, *i.e.*, $C-C<^{C}_{H}$ ; $c_4$, C–C; C–C; C–C, *i.e.*, $C-C<^{C}_{C}$

$$b_1' = (n - 1)b_1;\ b_2' = \sum_{r=1}^{n-1} A_r;\ b_3' = \sum_{r=1}^{n-1} B_r$$

where $A_r$ and $B_r$ are properties of the $r$th C–C bond and the summations are over all C–C bonds in the molecule. $A_r$ is the number of adjacent pairs of C–H ; C–C bonds which do not involve $r$, and $B_r$ is the number of adjacent C–C ; C–C bonds which do not involve $r$.

When these values are substituted in (8), the result is :

$$\Sigma y_j = -(n - 1)h + 2(b_1 + b_2\theta^2 + b_3\gamma_i^2)S - \{[(3n - 5)b_2 - 3b_3']h\theta^2 + [(3n - 7)b_3 - 3b_3']h\gamma_i^2 + 6(c_1 + c_2\theta^2 + c_3\gamma_i\theta^2 + c_4\gamma_i^3)\}S^2 \quad . \quad . \quad (9)$$

and the total electronic energy, obtained by substituting (9) in (7), is then the sum of first-order terms which are additive properties of the bonds present in the molecule, together with second-order terms which represent sums of interactions of adjacent bond pairs, and third-order terms corresponding to interaction energies for structural features of the kinds shown opposite the definitions of $c_1$, . . ., $c_4$, together with terms in $h$ which correspond to certain structural features which are not so easily visualised as interactions of bond orbitals.

Although the above results were derived specifically for hydrocarbons they apply equally to any other types of molecule when suitable additional parameters are included to represent the properties of orbitals for other kinds of bonds. The general result for the total energy still holds, *i.e.*, first-order additivity of " bond energies " with second-order correction terms from bond interaction energies.

*Electron Densities.*—In the general case where $S$ is not zero the formula (4) for electron densities must be modified, and, as shown by Lowdin (*J. Chem. Phys.*, 1950, **18**, 365), it is convenient to transform the coefficients of the molecular orbitals, $c_{rj}$, into another set, $C_{rj}$, by the relationship :

$$(\mathbf{1} + \mathbf{S})^{1/2}\mathbf{c} = \mathbf{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where the bold-face symbols represent the appropriate matrices, and the matrix $(\mathbf{1} + \mathbf{S})$ is the matrix of the overlap integrals. The modified definition for the electron density in the $r$th bond is then :

$$Q_r = 2\sum_{j=1}^{N} C_{rj}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which coincides with the definitions employed by Wheland, by Chirgwin and Coulson, and by Lowdin (*locc. cit.*) for the charge densities on atoms in the analogous treatment of conjugated systems.

As Lowdin observed, the matrix $\mathbf{C}$ is unitary, so the summation in (11) is unity, and all bonds thus have $Q_r = 2$. This uniformity of the charge distribution is again a consequence of all the molecular orbitals' being doubly filled ; in the case of the analogous treatment of conjugated systems where the molecular orbitals are not all filled, the uniformity of electron densities is no longer obtained, except in the special case of alternant hydrocarbon systems. In the present treatment the uniformity is valid for all types of molecules.

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# 534. *Studies in Spectroscopy. Part V.* Molecular Compound Formation with Polyhalogeno-iodo-compounds.*

By R. N. Haszeldine.

The ultra-violet spectrum of a polyfluoro-iodo-compound $R{\cdot}CF_2{\cdot}CF_2I$ is markedly dependent on the solvent used. The spectrum in light petroleum resembles that of the vapour, but in solvents such as $Bu^nCl$, $Bu^tCl$, $CH_3{\cdot}CO_2Et$, $Et_2O$, EtOH, or $Bu^n{\cdot}NH_2$, the absorption maximum moves up to 20 mμ towards the blue. For a particular solvent the shift in spectrum from that in light petroleum decreases in the series $R{\cdot}CF_2{\cdot}CF_2I$, $R{\cdot}CHF{\cdot}CF_2I$, $R{\cdot}CH_2{\cdot}CF_2I$, $R{\cdot}CF_2{\cdot}CH_2I$, $R{\cdot}CF_2{\cdot}CH_2{\cdot}CH_2I$, $R{\cdot}CH_2{\cdot}CH_2I$, *i.e.*, halogen substitution on both the α and the β carbon atom, but particularly on the former, is necessary for the maximum effect.

The shifts in spectra are compared with those for iodine in similar solvents. Molecular compound formation, (RI),B, between the neutral-molecule base B and the iodo-compound, RI (a weak Lewis acid), is suggested, with dative resonance structure of the type $(RI)^-{-}(B)^+$, and the implications of such complex formation on the reactivity of RI are discussed.

The ultra-violet absorption spectra of a series of fluorine-containing iodo-compounds were recorded and discussed in Part III (*J.*, 1953, 1764). The solvent was light petroleum, and it was shown that the spectrum in this solvent differed only slightly from the spectrum of the vapour. It has now been found that the spectra of polyhalogenoiodoalkanes containing halogen (other than iodine) on the α carbon atom in $\overset{\beta}{C}{\cdot}\overset{\alpha}{C}{\cdot}I$ vary greatly with the solvent. With heptafluoro-*n*-propyl iodide as an example, relevant data are given in Table 1. It is apparent that shifts in the absorption maximum of up to 20 mμ occur on

TABLE 1. *Ultra-violet spectrum of* $C_3F_7I$ *in various solvents.*

| Solvent | $\lambda_{max.}$ | $\varepsilon_{max.}$ | $\lambda_{min.}$ | $\varepsilon_{min.}$ | Solvent | $\lambda_{max.}$ | $\varepsilon_{max.}$ | $\lambda_{min.}$ | $\varepsilon_{min.}$ |
|---|---|---|---|---|---|---|---|---|---|
| Vapour ..... | 271 | 195 | 229 | 22 | $CH_3{\cdot}CO_2Et$ ... | 258—261 | 230 | — | — |
| Petrol * ..... | 271 | 240 | 215 | 13 | $Et_2O$ ..... | 257 | 250 | 235 | 200 |
| $CHCl_3$ ..... | 269·5 | 250 | — | — | Dioxan ..... | Inflexion 253—260, ε, 275 | | | |
| $Bu^nCl$ ..... | 267 | 240 | — | — | 50% Aq. EtOH | 254 | 200 | 220 | 100 |
| $Bu^tCl$ ..... | 265 | 230 | 232 | 130 | MeOH ..... | 251 | 235 | 225 | 160 |
| $H_2SO_4$ † ..... | 265 | — | 219 | — | EtOH ..... | 250·5 | 230 | 225·5 | 150 |
| $CH_3{\cdot}CO_2H$ ..... | 261—263 | 225 | — | — | | | | | |

* Light petroleum, b. p. 60—80°. † Saturated solution in conc. $H_2SO_4$.

change of solvent, and these shifts are larger than the usual slight solvent effect observed for unsubstituted alkyl iodides (cf. $Pr^nI$, Table 3: also the series of alkyl iodides in Part III, *loc. cit.*).

The maximum moves to shorter wave-length as the solvent changes from non-polar to polar in type, but this is not merely the effect of change in dielectric constant, since the maximum is at a longer wave-length in 50% aqueous ethanol than it is in anhydrous ethanol. The shift of the maximum is associated with solvents which contain an atom or atoms (*e.g.*, O, N) containing lone pairs of electrons, and if such a solvent is progressively diluted with petrol the maximum moves back to the longer wave-length. This is shown in Figs. 1 and 2, and in Table 2. For comparable *molar* dilutions, butylamine is more effective than ethanol, since the maximum almost disappears in the former solvent (Fig. 2). It should be noted that an isosbestic point is obtained in Figs. 1 and 2, and that double or abnormally broad maxima are not apparent in Fig. 1; the band envelope remains approximately the same in area and it is the position which is altered. The carbon–iodine bond in polyfluoroiodo-compounds undergoes homolytic fission readily but heterolytic fission only with difficulty (see papers in another series); true alkylammonium salt formation between, say, $C_3F_7I$, and a tertiary amine (*e.g.*, $NMe_3$) has not been achieved, although evidence other than that given below suggests that a weak complex can be formed.

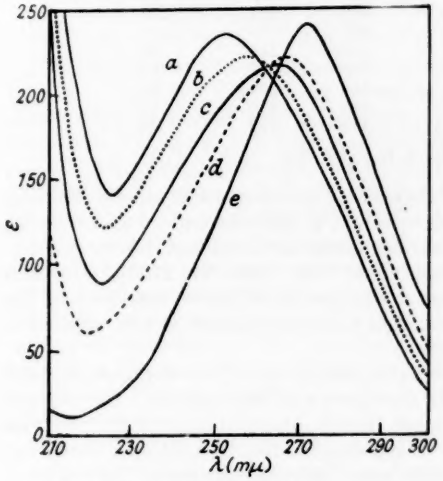
* Part IV, *J.*, 1953, 2525.

TABLE 2. *The effect of mixed solvents.*

| Solvent * | | $\lambda_{max.}$ | $\varepsilon_{max.}$ | $\lambda_{min.}$ | $\varepsilon_{min.}$ |
|---|---|---|---|---|---|
| EtOH–petrol | 100 : 1 | 250 | 230 | 226 | 160 |
| | 1 : 2 | 257 | 220 | 223 | 120 |
| | 1 : 5 | 264·5 | 220 | 222 | 90 |
| | 1 : 10 | 267 | 225 | 221 | 70 |
| | 1 : 100 | 271 | 240 | 215 | 15 |
| $Bu^n{\cdot}NH_2$–petrol | 1 : 50 | Slight inflexion 262—265 mμ, ε, 250 | | | |
| | 1 : 150 | Inflexion 262—265 mμ, ε, 250 | | | |
| | 1 : 250 | 268 | 225 | 244 | 160 |
| | 1 : 500 | 271 | 225 | 244 | 155 |
| Tetrahydropyran–petrol | 1 : 5 | 256 | 240 | — | — |
| | 1 : 10 | 263 | 235 | — | — |

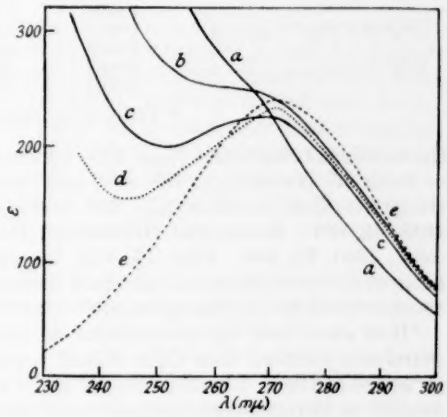
* Petrol = light petroleum, b. p. 60—80°.

FIG. 1. *Ultra-violet spectrum of heptafluoroiodopropane in ethanol–light petroleum.*




Solvents: *a*, Pure ethanol.
*b*, EtOH–petrol 1 : 2.
*c*, ,, 1 : 5.
*d*, ,, 1 : 10.
*e*, Light petroleum (100%).

FIG. 2. *Ultra-violet spectrum of heptafluoroiodopropane in* n*-butylamine–light petroleum.*




Solvents: *a*, $Bu^n{\cdot}NH_2$–petrol 1 : 50.
*b*, ,, 1 : 150.
*c*, ,, 1 : 250
*d*, ,, 1 : 500.
*e*, Light petroleum (100%).

That the marked solvent effect depends on both α and β substitution in the iodo-compound $\overset{\beta}{C}{\cdot}\overset{\alpha}{C}{\cdot}I$ is shown in Table 3. These results may be analysed as follows:

*Compounds of the type* $R{\cdot}CH_2I$ (R = *alkyl, polyfluoroalkyl*). The solvent effect, Δ [$\lambda_{max.}$ (petrol) − $\lambda_{max.}$ (EtOH)], is very similar to that in propyl iodide (3—4 mμ) when R = $CF_3{\cdot}CH_2$ or $CF_3$; *i.e.*, if only hydrogen is present on the α carbon atom of the iodo-compound, β- and γ-substituents do not have a marked influence.

*Compounds of the type* $R{\cdot}CH_2{\cdot}CF_2I$ *or* $RR'CH{\cdot}CF_2I$ (R = H, *alkyl, or polyfluoroalkyl*, R = H *or alkyl, but not perfluoroalkyl*). When the compound has fluorine on the α-carbon atom but does not contain halogen on the β-carbon atom, the solvent effect is appreciably increased (5—8 mμ; see $CF_3{\cdot}CHMe{\cdot}CF_2I$, $CF_3{\cdot}CH_2{\cdot}CF_2I$, Table 3). Substitution of fluorine at the α-carbon atom thus determines the value of Δ more than does substitution at the β-carbon atom, but that β-substitution has an effect is shown below.

*Compounds of the type* $R{\cdot}CHF{\cdot}CF_2I$ (R = *fluorine or polyfluoroalkyl*). Here the solvent effect becomes large (10—12 mμ), but it is noteworthy that the highest value of Δ (20 mμ) is obtained when the β-carbon atom carries no hydrogen atom or alkyl group, but only

fluorine or perfluoroalkyl groups (*e.g.*, $C_3F_7I$). The effect on Δ of replacement of the β-hydrogen atom in $CF_3{\cdot}CHF{\cdot}CF_2I$ by fluorine is much larger than might have been expected from comparison of the spectra of $CF_3{\cdot}CH_2{\cdot}CF_2I$ and $CF_3{\cdot}CHF{\cdot}CF_2I$.

The effect of solvent on the absorption spectrum of the polyhalogenoiodo-compounds is very similar to that on the spectrum of iodine. It is well known that iodine vapour and iodine solutions in non-polar solvents ($CCl_4$, $CS_2$, light petroleum, etc.) have similar spectra,

TABLE 3.

| Compound | Solvent * | $\lambda_{max.}$ | $\varepsilon_{max.}$ | $\lambda_{min.}$ | $\varepsilon_{min.}$ | Δ |
|---|---|---|---|---|---|---|
| $C_3F_7I$ | Petrol | 271 | 240 | 215 | 13 | 20 |
| | EtOH | 250·5 | 230 | 225·5 | 150 | |
| $CF_3{\cdot}CHF{\cdot}CF_2I$ | Petrol | 268 | 255 | 223 | 50 | 12 |
| | EtOH | 256 | 230 | 221 | 88 | |
| $CHF_2{\cdot}CF_2I$ | Petrol | 265 | 255 | 215 | 14 | 10 |
| | EtOH | 255 | 255 | 222 | 120 | |
| $CF_3{\cdot}CH_2{\cdot}CF_2I$ | Petrol | 271 | 290 | 219 | 25 | 8 |
| | EtOH | 263 | 280 | 219 | 70 | |
| $CF_3{\cdot}CHMe{\cdot}CF_2I$ | Petrol | 270 | 330 | 238 | 80 | 5 |
| | EtOH | 265 | 300 | 233 | 100 | |
| $CF_3{\cdot}CH_2I$ | Petrol | 262 | 265 | — | — | 4 |
| | EtOH | 258 | 255 | 214 | 30 | |
| $CF_3{\cdot}CH_2{\cdot}CH_2I$ | Petrol | 261 | 370 | 213 | 20 | 3 |
| | EtOH | 258 | 350 | 209 | 25 | |
| $Pr^nI$ | Petrol | 258 | 465 | 210 | 15 | 3 |
| | EtOH | 254·5 | 485 | 212 | 45 | |

* Petrol = light petroleum, b. p. 60—80°.

the solutions being violet ($\lambda_{max.}$ 495—540 mμ), whereas iodine solutions in ethers, alcohols, or water are brown ($\lambda_{max.}$ 460—480 mμ); iodine solutions in benzene and methylbenzenes are intermediate in colour ($\lambda_{max.}$ 490—500 mμ) (see Kleinberg and Davidson, *Chem. Reviews*, 1948, **42**, 601; Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703). Mulliken (*ibid.*, 1950, **72**, 600; 1952, **74**, 811) has discussed the spectra of iodine solutions on the basis of electron-donor and -acceptor interaction, and a similar concept is now applied to the spectra of the polyhalogenoiodo-compounds.

It is clear that the true spectra of the iodo-compounds are those obtained in light petroleum solution, since these closely resemble the spectra of the vapours; the valency structure of the C–I bond in the RI molecule must thus be changed appreciably when an oxygen- or nitrogen-containing solvent is used. It is suggested that in solution in a neutral-molecule ("onium") base B ($NR'_3$, $OR'_2$, R'OH, etc.) the iodo-compound RI forms a 1 : 1 (probably) or 1 : *n* molecular complex of the donor–acceptor type, the donated electron in the structure $\psi[B^+{-}(RI)^-]$ being derived from the lone pair of electrons in B. The wave-functions are mainly of the van der Waals [(RI)·(B)] structure such as (I) or (II) (the latter being of the type postulated for iodine by Mulliken); *i.e.*, transfer of an electron from B to RI with formation of a *weak* covalent bond between the odd electron of $B^+$ and $(RI)^-$, with resonance in the excited state involving structures for (II) such as (III) or (IV). An alcohol R'OH is taken as example of B.

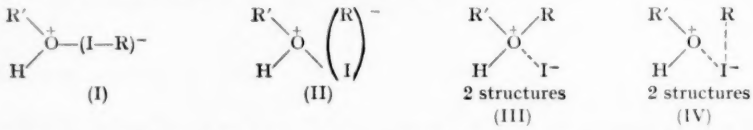



Table 3 shows that the shift in $\lambda_{max.}$ increases (for the particular pair of solvents studied) as the inductive effect of R in RI increases, *i.e.*, as the number of electronegative substituents on the α-carbon atom of RI increases. In a weak molecular complex of the type postulated above, the more positive the α-carbon atom in RI, the more positive will be the iodine atom, and the ease of charge transfer from the oxygen or nitrogen of the base should increase, *i.e.*, the more positive the iodine, the greater should be the shift in absorption spectrum. RI thus acts as a neutral-molecule Lewis acid by virtue of the incompletely satisfied electronegativity of its iodine atom. It is emphasised that there is only a slight

shift in the spectrum (3—4 mμ) of an unsubstituted iodo-compound on change from light petroleum to ethanol (see Table 3 and Part III, *loc. cit.*).

From consideration of Table 1 it would appear that an alkyl chloride containing a lone chlorine atom can act as a Lewis base. The shift in absorption maximum of heptafluoroiodopropane from that in light petroleum is 4 mμ with *n*-butyl chloride and 6 mμ with *tert.*-butyl chloride. Loose complexes ($Bu^nCl$),($C_3F_7I$) and ($Bu^tCl$),($C_3F_7I$) involving the lone pair of electrons on the chlorine atom are indicated.

The solubility of heptafluoroiodopropane in concentrated sulphuric acid is limited, but a distinct shift in spectrum (6 mμ) is apparent. With acetic acid and ethyl acetate shifts of 9—10 and 12—13 mμ relatively to light petroleum are obtained. Here the complexes could be either of two types (or both): (*a*) complex formation involving the OH or OEt group of the acid or ester as discussed above for alcohols and ethers, and (*b*) complex formation involving the carbonyl group (*e.g.*, V or VI).

(V) $\left(\begin{matrix} CH_3 \\ \diagdown \\ C{=}O \\ \diagup \\ EtO \end{matrix}\right)$,(RI)

(VI) $\begin{matrix} CH_3 \\ \diagdown \\ C{=}O \\ \diagup \\ EtO \end{matrix}\!\!\begin{matrix} R \\ \diagup \\ \\ \diagdown \\ I^- \end{matrix}$

Mulliken has pointed out that the ease of transfer of the non-bonding electron from the base B to the Lewis acid should depend on the ionisation potential of B, and the stability of the complex should vary accordingly. For water, ethyl chloride, ethanol, ethyl ether, and trimethylamine, the ionisation potentials are 12·61, 10·89, 10·7, 10·2, and 9·4 ev, respectively (Price, *Chem. Reviews*, 1947, **41**, 257) and one would expect base strength to increase in this order. Tables 1 and 2 show that the shifts in absorption spectra are in fact $Bu{\cdot}NH_2 > EtOH > 50\%\ EtOH > Et_2O > BuCl$. The amine is the most efficient of all in shifting the maximum to shorter wave-length and in fact the maximum almost disappears (Fig. 2); here, a relatively stable complex is formed whose bonding tends towards that of a tetra-alkylammonium iodide in type.

Table 1 and Figs. 1 and 2 show that there is little change in extinction coefficient on change of solvent; *i.e.*, if a spectral transition corresponding to *intermolecular charge transfer* in the molecular complex occurs in the 215—350-mμ region studied it does not lead to high-intensity absorption of the type observed near 300 mμ for the iodine–aromatic solvent complexes.

In Part III (*loc. cit.*) the absorption of a polyfluoroiodo-compound in light petroleum was shown to lie at much longer wave-length than that of the corresponding unsubstituted compound and this was interpreted as indicating a decrease in carbon–iodine bond dissociation energy caused by increase in stability of the free radical R. The present study has shown that in a basic solvent such as ethanol the carbon–iodine absorption is very similar to that of an unsubstituted primary alkyl iodide in *either* alcohol *or* light petroleum. If in the basic solvent the fluoro-iodide is part of a complex, it is suggested that by use of such a complex, where the carbon–iodine bond approaches more to that in, say, ethyl iodide, in character, it might be possible to effect synthetic reactions involving ionic intermediates which are difficult, if not impossible, to effect with polyfluoroiodo-compounds in solvents where complex formation cannot occur. Experiments to test this hypothesis are in progress, but there is already some evidence from published work that this might be so. In another series (*J.*, 1952, 3423 *et seq.*) the preparation of the Grignard compound $C_3F_7{\cdot}MgI$ was shown to be possible in ethyl ether and triethylamine, but impossible in the non-basic solvents $(C_4F_9)_2O$ or $N(C_3F_7)_3$; further, the yield of the Grignard compound was increased if the more basic solvent tetrahydropyran were used; *i.e.*, possibly complex formation first occurs and makes the fluoro-iodide more susceptible to reaction with magnesium.

The evidence presented above thus shows that a polyfluoroalkyl group R in an iodo-compound RI acts like a pseudohalogen, and that solutions of RI in basic solvents yield molecular compounds of the type which have long been known to exist between halogen molecules and organic compounds and between the $Ag^+$ ion and aromatic or unsaturated compounds.

### Experimental

*Compounds.*—The iodo-compounds were prepared in this laboratory, and the methods used and the physical properties have been, or will be, reported in other series (Haszeldine, *J.*, 1949, 2856 *et seq.*; 1951, 584 *et seq.*; 1952, 1504 *et seq.*). The compounds $CF_3 \cdot CHF \cdot CF_2I$, $CHF_2 \cdot CF_2I$, $CF_3 \cdot CH_2 \cdot CF_2I$, and $CF_3 \cdot CH_2I$ were kindly prepared by Mr. B. R. Steele.

*Apparatus.*—A Beckman Model DU and a Unicam Spectrophotometer were used, with 1-, 2-, or 10-cm. cells as required. The spectra were usually determined in duplicate, and average values are reported. The wave-length was measured to 0·25 mμ in the maximum, minimum, or inflexion areas.

*Solvents.*—Light petroleum (b. p. 60—80°) was purified by treatment with fuming sulphuric acid and alkaline permanganate. It showed 43% transmission at 210 mμ. Ethanol (95%; benzene-free) was dried by distillation from calcium oxide and then showed 42% transmission at 210 mμ.

Other solvents were thoroughly dried and purified by conventional methods. The following transmissions were shown: $CHCl_3$, 265 mμ, 95%; 255 mμ, 70%. $H_2SO_4$, 250 mμ, 70%; 210 mμ, 55%. $Bu^nCl$, 250 mμ, 90%; 235 mμ, 70%. $Bu^tCl$, 270 mμ, 80%; 250 mμ, 62%. $CH_3 \cdot CO_2H$, 260 mμ, 80%; 250 mμ, 30%. $CH_3 \cdot CO_2Et$, 270 mμ, 65%; 260 mμ, 60%. $Et_2O$, 220 mμ, 65%; 210 mμ, 45%. Dioxan, 270 mμ, 90%; 250 mμ, 60%. MeOH, 250 mμ, 90%; 220 mμ, 50%. $Bu^n \cdot NH_2$–light petroleum, 1 : 50, 250 mμ, 50%; 242 mμ, 40%. 1 : 150, 250 mμ, 96%; 240 mμ, 55%. 1 : 250, 250 mμ, 100%; 240 mμ, 75%. 1 : 500, 240 mμ, 95%; 234 mμ, 45%. Tetrahydropyran–light petroleum, 1 : 5, 260 mμ, 65%; 242 mμ, 40%. 1 : 10, 260 mμ, 81%; 240 mμ, 60%.

Pure butylamine and tetrahydropyran do not transmit sufficient light in the 250—280-mμ region to make them suitable as solvents, and dilution with light petroleum in the *volume* ratio shown above was therefore used (Table 2; Figs. 1 and 2).

University Chemical Laboratory, Cambridge. [*Received, March 23rd*, 1953.]

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## 535. *Simple Analogues of Cortisone. Part II.* Some Monocyclic Compounds.*

By J. D. Billimoria.

The *cis*- and the *trans*-1-ethynyl-2-methyl*cyclo*hexanol (I) were hydrated to the *cis*- and *trans*-1-acetyl-2-methyl*cyclo*hexanols (II). The latter were converted via their bromides (III) into *cis*- and *trans*-1-glycolloyl-2-methyl*cyclo*hexanols (IV). Anionotropic rearrangement of 1-vinyl-2-methyl*cyclo*hexanol (VI) followed by oxidation gave 1-acetoxyacetyl-2-methyl*cyclo*hexanol (VIII) isolated as semicarbazone. Ethyl α-chloro-1-hydroxy-2-methyl*cyclo*hexylacetate (X) was found to be an unsuitable starting material in preliminary experiments as subsequent dehydration probably occurs in the *cyclo*hexane ring in preference to the side chain. The infra-red spectra of 1-glycolloyl*cyclo*hexanol and the *cis*- and *trans*-forms of 1-glycolloyl-2-methyl*cyclo*hexanol are recorded.

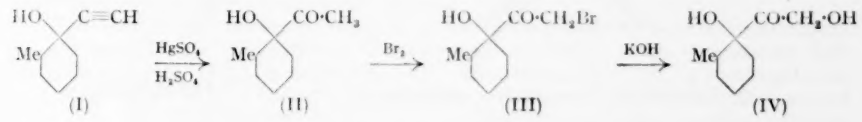
A previous communication * recorded the preparation of 1-glycolloyl*cyclo*hexanol from 1-hydroxy*cyclo*hexanecarboxylic acid. An attempt similarly to obtain 1-glycolloyl-2-methyl*cyclo*hexanol was abandoned because of difficulties in obtaining a stereochemically pure 1-hydroxy-2-methyl*cyclo*hexanecarboxylic acid. 2-Methyl*cyclo*hexanone cyanohydrin, obtained by the action of aqueous potassium cyanide on the hydrogen sulphite adduct of the ketone, gave only ammonium chloride and 2-methyl*cyclo*hexanone on acid hydrolysis. The cyanohydrin also behaved abnormally on treatment with methylmagnesium iodide, yielding a compound $C_8H_{15}O$ (probably 1 : 2-dimethyl*cyclo*hexanol; see Experimental section).

Milas, MacDonald, and Black (*J. Amer. Chem. Soc.*, 1948, **70**, 1829) and Heilbron,

* Part I, *J.*, 1951, 3067.

Jones, Lewis, and Weedon (*J.*, 1949, 2023) have described the preparation of the solid and the liquid isomer of 1-ethynyl-2-methyl*cyclo*hexanol. The *cis*- and *trans*-configurations of these alcohols with respect to the methyl group are unknown, and for convenience the solid isomer and all compounds obtained from it are prefixed (*sol.*), and the liquid isomer and compounds from it correspondingly (*liq.*).

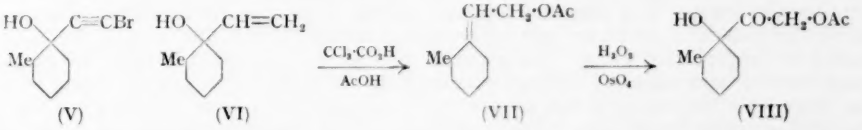
(*sol.*)-1-Ethynyl-2-methyl*cyclo*hexanol on oxidation with potassium permanganate furnished (*sol.*)-1-hydroxy-2-methyl*cyclo*hexanecarboxylic acid only in low yield, but no acidic fraction could be isolated by similar oxidation of the (*liq.*)-alcohol. The alcohols were, however, converted by a more convenient route into the desired keto-alcohols.




The (*sol.*)- and (*liq.*)-alcohols (I) were roughly separated and each was hydrated with mercuric sulphate in aqueous sulphuric acid. The mercury complex which separated during hydration often decomposed violently even at 0°, in nitrogen, but in the presence of carbon tetrachloride this decomposition was avoided. The (*sol.*)- and the (*liq.*)-form of the ketone (II) were completely separated by a fractionation of their semicarbazones from ethanol. Regeneration gave a crystalline (*sol.*)- and a pure liquid (*liq.*)-1-acetyl-2-methyl*cyclo*hexanol.

Acid-catalysed bromination of the respective ketones gave a solid (*sol.*)-1-bromoacetyl-2-methyl*cyclo*hexanol (III) and a liquid (*liq.*)-bromide (III). Hydrolysis of the (*sol.*)-form directly gave the pure crystalline (*sol.*)-1-glycolloyl-2-methyl*cyclo*hexanol (IV) whereas the corresponding liquid (*liq.*)-compound was obtained only through its semicarbazone. The latter derivatives were formed with difficulty and in low yield whereas the thiosemicarbazones were readily obtained. The bromides (III) gave crystalline quaternary salts with pyridine, the keto-alcohols readily reduced alkaline copper sulphate, and all derivatives of the (*sol.*)-series depressed the m. p. of the corresponding (*liq.*)-compounds.

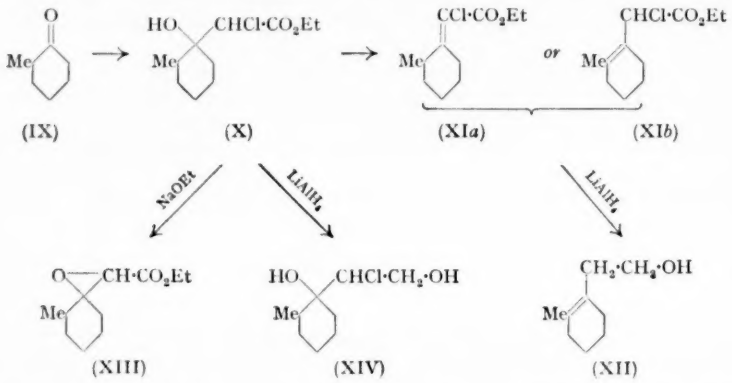
The (*sol.*)-1-ethynyl compound with aqueous potassium hypobromite readily furnished the (*sol.*)-1-bromoethynyl-2-methyl*cyclo*hexanol (V) but attempts to convert this directly into the bromide (III) were unsuccessful.




Semihydrogenation of (*liq.*)-(I) and treatment of the (*liq.*)-(VI) with trichloroacetic acid in acetic anhydride gave 2-2′-methyl*cyclo*hexylidene-ethyl acetate (VII). Oxidation of this with anhydrous hydrogen peroxide in *tert.*-butanol, catalysed by osmium tetroxide, gave a mixture from which (*liq.*)-1-acetoxyacetyl-2-methyl*cyclo*hexanol (VIII) was isolated in small yield.

2-Methyl*cyclo*hexanone (IX) was further condensed with ethyl dichloroacetate in the presence of magnesium amalgam and a trace of iodine as promoter, to yield ethyl α-chloro-1-hydroxy-2-methyl*cyclo*hexylacetate (X). This with alcoholic sodium ethoxide gave the epoxide (XIII) whilst with lithium aluminium hydride it gave 2-chloro-2-(1-hydroxy-2-methyl*cyclo*hexyl)ethanol (XIV). Further, the α-chloro-ester (X) on dehydration with phosphorus oxychloride in pyridine gave the unsaturated ester (XI*a* or XI*b*). As reduction with lithium aluminium hydride gave chlorine-free, unsaturated alcohol, the material could not be used for further work. Wagner and Moore (*J. Amer. Chem. Soc.*, 1949, **71**, 4160) have reduced methyl 20-bromo-3β-hydroxy-17-pregnen-21-oate (analogous structure to XI*a*) with lithium aluminium hydride to the corresponding unsaturated alcohol

without the loss of the tertiary halogen; the above dehydration product may therefore have the structure (XI*b*), and the reduction product would then be (XII). Further work




on these lines is being pursued. The infra-red spectra * of three keto-alcohols show the following bands:

| | C=O, cm.$^{-1}$ | Ring OH, cm.$^{-1}$ | Ketol OH, cm.$^{-1}$ |
|---|---|---|---|
| (*A*) 1-Glycolloyl*cyclo*hexanol ..... | 1710 (90) | 3400—3200 (90) | 2910 (82) |
| (*B*) (*sol.*)-1-Glycolloyl-2-methyl*cyclo*hexanol ..... | 1710 (93) | 3500 (82) | 2910 (92) |
| (*C*) (*liq.*)-1-Glycolloyl-2-methyl*cyclo*hexanol ..... | 1700 (94) | 3575 (70) | 2910 (92) |

(Values in parentheses are % absorption.)

The ring hydroxy-group and the ketol-hydroxy-groups in (*A*) both show strong hydrogen bonding, whilst in (*B*) and (*C*) this effect is only observed in the ketol-hydroxy-groups. Compounds (*B*) and (*C*) show almost identical bands and their spectra differ mainly in the region 800—1200 cm.$^{-1}$.

## Experimental

The microanalyses were carried out by Dr. Sobotka, University of Graz, and in the Microanalytical Laboratory, Organic Chemistry Department, Imperial College (Mr. F. H. Oliver).

2-*Methyl*cyclo*hexanone Cyanohydrin*.—2-Methyl*cyclo*hexanone (10 g.) was added dropwise with vigorous stirring to a saturated aqueous solution of sodium metabisulphite (20 g.), the mixture set aside at 5° for 24 hr., and the crystalline adduct (18 g.; after vacuum drying) then washed thoroughly with water. The material (10·3 g.) was suspended in ether (50 c.c.) and water (10 c.c.), and aqueous potassium cyanide (5 g.) was added with stirring during 15 min. The ether layer was removed, the aqueous layer extracted with ether (5 × 10 c.c.), and the combined extracts (dried with $Na_2SO_4$) distilled, giving 2-*methyl*cyclo*hexanone cyanohydrin* (4·4 g.) as a viscous oil, b. p. 68°/10$^{-6}$ mm. (bath temp. 120°), $n_D^{22}$ 1·4544 (Found: C, 69·1; H, 9·35; N, 10·1. $C_8H_{13}ON$ requires C, 68·9; H, 9·3; N, 10·2%).

*Reaction of the Cyanohydrin with Methylmagnesium Iodide*.—The cyanohydrin (10 g.) was added gradually with stirring to an ethereal solution (500 c.c.) of methylmagnesium iodide [from magnesium (4 g.) and methyl iodide (30 g.)], and the solution was refluxed for 1 hr. After solation, the crude compound was heated under reflux (0·5 hr.) with hydrochloric acid (10%; 100 c.c.), extracted with ether, and distilled, giving 1 : 2-dimethyl*cyclo*hexanol (?) (8 g.), b. p. 55°/8 mm., 168°/760 mm., $n_D^{21}$ 1·4622. The authentic compound (Found: C, 75·3; H, 12·5. Calc. for $C_8H_{16}O$: C, 75·0; H, 12·5%) prepared as above from 2-methyl*cyclo*hexanone had the same physical constants (Signaigo and Cramer, *J. Amer. Chem. Soc.*, 1933, **55**, 3330, give b. p. 64°/9 mm., 169°/760 mm., $n_D^{20}$ 1·4620).

(sol.)- *and* (liq.)-1-*Ethynyl*-2-*methyl*cyclo*hexanols*.—The method used was essentially that of Heilbron *et al.* (*loc. cit.*), Nieuwland's catalyst (Vaughn, Vogt, and Nieuwland, *J. Amer. Chem.*

* These will appear in Sadtler's "Catalog of Infra-red Spectrograms," Philadelphia. They were determined on a Baird double-beam instrument, that of 1-glycolloyl*cyclo*hexanol as a melt, those of the 1-glycolloyl-2-methyl*cyclo*hexanols on 10% solutions in chloroform.

*Soc.*, 1934, **56**, 2120) being used for the formation of sodium acetylide. From 2-methyl*cyclo*hexanone (1000 g.), sodium acetylide [from sodium (215 g.)], and liquid ammonia (5 l.), the mixed isomers (1000 g.), b. p. 74—78°/15 mm., were obtained. After purification through the silver salt and regeneration with ammonium thiocyanate at room temperature, the ethynyl compound (900 g.) was kept at 0° for 24 hr. whereupon a portion crystallised and was rapidly separated in a filtration centrifuge. A repetition of this crystallisation gave the solid (225 g., 33%) and the liquid (674 g., 66%) isomer. The yields were reproducible in several experiments. After crystallisation from light petroleum (b. p. 40—60°) the solid form was obtained as needles, m. p. 59—60° (Found: C, 78·3; H, 10·2. Calc. for $C_9H_{14}O$: C, 78·3; H, 10·15%). After redistillation the liquid isomer had b. p. 76°/15 mm., $n_D^{23}$ 1·4689 (Found: C, 78·5; H, 10·2%).

(sol.)-1-*Hydroxy*-2-*methyl*cyclo*hexanecarboxylic Acid.*—(*sol.*)-1-Ethynyl-2-methyl*cyclo*hexanol (10 g.) in acetone (100 c.c.) was treated dropwise with stirring at room temperature with potassium permanganate (13 g.) in water (200 c.c.). After being stirred for 12 hr. the mixture was heated on the steam bath (1 hr.), the filtered solution evaporated, and the residue dissolved in a little ether. This solution was then shaken with saturated aqueous sodium hydrogen carbonate, and from the ether layer unchanged material (5 g.) was recovered.

The aqueous layer was acidified, treated with salt, and re-extracted with ether. Evaporation of the solvent and crystallisation of the residue from benzene gave (sol.)-1-*hydroxy*-2-*methyl*cyclo*hexanecarboxylic acid* (2·5 g.), needles, m. p. 109° (Found: C, 61·0; H, 9·1. $C_8H_{14}O_3$ requires C, 60·8; H, 8·9%).

(sol.)-1-*Bromoethynyl*-2-*methyl*cyclo*hexanol.*—(*sol.*)-1-Ethynyl-2-methyl*cyclo*hexanol (13·8 g.) in light petroleum (100 c.c.; b. p. 40—60°) was shaken for 6 hr. with an aqueous solution (200 c.c.) containing potassium hypobromite (7·4%) and potassium hydroxide (11·2%) (cf. Strauss, Kollek, and Heyn, *Ber.*, 1930, **63**, 1868). The aqueous layer was extracted with light petroleum (4 × 100 c.c.; b. p. 40—60°), and the combined organic layers were dried ($Na_2SO_4$) and evaporated giving (sol.)-1-*bromoethynyl*-2-*methyl*cyclo*hexanol* (18 g.), needles, m. p. 69—70° [from light petroleum (b. p. 40—60°)] (Found: C, 50·1; H, 6·1; Br, 36·5. $C_9H_{13}OBr$ requires C, 49·8; H, 6·0; Br, 36·9%).

(sol.)-1-*Acetyl*-2-*methyl*cyclo*hexanol.*—(*sol.*)-1-Ethynyl-2-methyl*cyclo*hexanol (100 g.) in carbon tetrachloride (250 c.c.) was added dropwise with stirring to a solution of mercuric sulphate (26·3 g.) in sulphuric acid (70 g.) and water (600 c.c.), and the reaction mixture kept at 15° for 2 hr. The aqueous layer was steam-distilled for 3 hr., the organic layer (which had been kept at 0°) being gradually added. The distillate was treated with salt, the organic layer separated, and the aqueous layer extracted with carbon tetrachloride (5 × 100 c.c.). The combined extracts were dried ($Na_2SO_4$), the solvent was removed and the residue was distilled, giving the ketone (96 g.), b. p. 81—82°/12 mm. The (sol.)-*semicarbazone* (prepared in pyridine) formed needles, m. p. 229—230° (after 2 crystallisations from ethanol) (Found: C, 56·6; H, 8·9; N, 19·7. $C_{10}H_{19}O_2N_3$ requires C, 56·3; H, 8·9; N, 19·7%). When shaken in light petroleum suspension (500 c.c.; b. p. 40—60°) for 6 hr. with aqueous sulphuric acid (10%) this gave (sol.)-1-*acetyl*-2-*methyl*cyclo*hexanol* (72 g.), b. p. 87°/12 mm. (after purification and distillation), which solidified when cooled at 0° for 4 hr. and then formed needles, m. p. 36° [from light petroleum (b. p. 40—60°)] (Found: C, 69·2; H, 10·3. $C_9H_{16}O_2$ requires C, 69·3; H, 10·3%).

(liq.)-1-*Acetyl*-2-*methyl*cyclo*hexanol.*—This was similarly obtained by the hydration of the (*liq.*)-1-ethynyl-2-methyl*cyclo*hexanol (200 g.) with mercuric sulphate (52·5 g.) in sulphuric acid (140 c.c.) and water (1200 c.c.). After three crystallisations from ethanol the (liq.)-*semicarbazone* was obtained as needles, m. p. 218—219° [depressed to 205° when melted in admixture with the (*sol.*)-semicarbazone] (Found: C, 56·6; H, 8·9; N, 19·7%).

The pure regenerated (*liq.*)-ketone (170 g.) had b. p. 92°/10 mm., $n_D^{18}$ 1·4635 (Found: C, 69·7; H, 10·4%).

(sol.)-1-*Bromoacetyl*-2-*methyl*cyclo*hexanol.*—(*sol.*)-1-Acetyl-2-methyl*cyclo*hexanol (46·8 g.) in chloroform (500 c.c.) was added in one portion to a solution of bromine (16 c.c.) in chloroform (500 c.c.) containing freshly distilled hydrogen bromide in acetic acid (1 c.c. of 30%). After 0·5 hr. the solution was poured into ice–water (1 l.) and neutralised with sodium hydrogen carbonate. The solution was extracted with chloroform (5 × 100 c.c.), the extracts were dried ($Na_2SO_4$), and the solvent evaporated *in vacuo* (40°). Crystallisation of the residue from light petroleum (b. p. 40—60°) at −30° gave (sol.)-1-*bromoacetyl*-2-*methyl*cyclo*hexanol* (40 g.), as needles, m. p. 68—69° (soon becoming violet on exposure to air at room temperature) (Found: C, 45·7; H, 6·5; Br, 34·1. $C_9H_{15}O_2Br$ requires C, 45·9; H, 6·4; Br, 34·0%).

(liq.)-1-*Bromoacetyl*-2-*methyl*cyclo*hexanol*.—A similar bromination of (*liq.*)-1-acetyl-2-methyl*cyclo*hexanol (30 g.) yielded the liquid (liq.)-*bromide* (27 g.) on evaporative distillation from a wide-bore retort (bath temp. 75—80°) at $10^{-6}$ mm. (Found : C, 45·8; H, 6·3; Br, 33·7%).

*Pyridine Adducts of the Bromides*.—A solution of the (*sol.*)-bromide (2 g.) in pyridine (3 c.c.) was diluted with dry ether (10 c.c.) and set aside at 0° for 24 hr. The precipitate (2·6 g.) was dissolved in a little warm methanol, and the solution diluted with ether, the (sol.)-*pyridine adduct* forming flat prisms, m. p. 188—190° (decomp.) (Found : C, 53·6; H, 6·2; N, 4·3; Br, 25·0. $C_{14}H_{20}O_3NBr$ requires C, 53·5; H, 6·35; N, 4·5; Br, 25·4%).

The (liq.)-*adduct*, similarly obtained, had m. p. 202—203°, depressed to 170° on admixture with the (*sol.*)-adduct (Found : C, 53·8; H, 6·2; N, 5·2; Br, 25·7%).

(sol.)- *and* (liq.)-1-*Glycolloyl*-2-*methyl*cyclo*hexanol*.—The (*sol.*)-bromide (23·5 g.) was dissolved in aqueous ethanol (60%; 235 c.c.), and potassium hydroxide (5·8 g.) in aqueous ethanol (60%; 100 c.c.) added under nitrogen with stirring in 5-c.c. portions, at such a rate that the alkali was neutralised (phenolphthalein) before each subsequent addition. After the last addition, the solution was made just acid with a trace of aqueous hydrogen chloride and then evaporated to dryness *in vacuo* (at 40°), and the oily residue dissolved in ether. The ethereal solution was dried ($Na_2SO_4$), the solvent evaporated, and the crude residue triturated with light petroleum (b. p. 40—60°). (sol.)-1-*Glycolloyl*-2-*methyl*cyclo*hexanol* formed needles (from ether), m. p. 79—80° (Found : C, 63·2; H, 9·5. $C_9H_{16}O_3$ requires C, 62·8; H, 9·3%).

The (*liq.*)-bromide (23·5 g.) on similar hydrolysis gave the crude (*liq.*)-keto-alcohol (11 g.), whose *semicarbazone* (prepared in pyridine–water) was obtained as micro-needles (from methanol) (11 g.), m. p. 199—201° (Found : C, 52·3; H, 8·3; N, 18·4. $C_{10}H_{19}O_3N_3$ requires C, 52·4; H, 8·2; N, 18·1%).

Heating of the semicarbazone (11 g.) with hydrochloric acid (10%; 50 c.c.) on the steam-bath for 15 min. (nitrogen atmosphere), evaporation *in vacuo* at 70°, and evaporative distillation in a high vacuum at $10^{-6}$ mm. (bath temp. 75°) gave (liq.)-1-*glycolloyl*-2-*methyl*cyclo*hexanol*, $n_D^{21\cdot5}$ 1·4722 (Found : C, 63·0; H, 9·5%).

*The thiosemicarbazones*. The (*sol.*)-keto-alcohol (1·8 g.), thiosemicarbazide (1 g.), aqueous ethanol (60%; 35 c.c.), and a trace of acetic acid were heated under reflux for 2 hr. On cooling and dilution with a little water the (*sol.*)-thiosemicarbazone separated. This formed pale yellow needles, m. p. 210°, from methanol (Found : C, 49·4; H, 7·7; N, 17·2; S, 13·4. $C_{10}H_{19}O_2N_3S$ requires C, 49·0; H, 7·8; N, 17·1; S, 13·1%). The (liq.)-*thiosemicarbazone* was similarly obtained as yellow needles, m. p. 220°, from aqueous methanol (Found : C, 49·0; H, 7·9; N, 17·1; S, 13·2%).

(liq.)-2-*Methyl*-1-*vinyl*cyclo*hexanol*.—(*liq.*)-1-Ethynyl-2-methyl*cyclo*hexanol (138 g.) in ethanol (500 c.c.) was hydrogenated in the presence of palladium–strontium carbonate (10 g.; containing 2½% of Pd) (22·2 l. of hydrogen were absorbed). The filtered solution was fractionated through a 12″ column, giving (liq.)-2-*methyl*-1-*vinyl*cyclo*hexanol* (119 g.), b. p. 69°/7 mm., $n_D^{21}$ 1·4711 (Found : C, 77·0; H, 11·6. $C_9H_{16}O$ requires C, 77·1; H, 11·4%).

2-2′-*Methyl*cyclo*hexylidene-ethyl Acetate*.—The vinyl*cyclo*hexanol (121 g.), acetic anhydride (450 c.c.), and trichloroacetic acid (150 g.) were heated at 55° for 2 hr., and then poured into ice–water (2000 c.c.). After 3 hr. the mixture was neutralised ($NaHCO_3$) and extracted with ether. Fractionation of the extract through a 12″ column gave 2-2′-*methyl*cyclo*hexylidene-ethyl acetate* (43 g.), b. p. 98—100°/8 mm., $n_D^{23}$ 1·4492 (Found : C, 72·3; H, 10·0. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·9%).

*Oxidation of* 2-2′-*Methyl*cyclo*hexylidene-ethyl Acetate*.—An anhydrous solution of hydrogen peroxide in *tert.*-butanol was prepared by dissolving 80% aqueous hydrogen peroxide in the alcohol and adding a calculated quantity of butyl borate.

Osmium tetroxide (0·05 g.) was added to a stirred mixture of 2-2′-methyl*cyclo*hexylidene-ethyl acetate (7 g.) in *tert.*-butanol (40 c.c.) and the hydrogen peroxide solution (11·1 c.c.), and after 36 hr. the solvent was removed under reduced pressure (40°) and the residue boiled with aqueous sodium sulphite (10 g. in 100 c.c.). Extraction with ether gave a liquid (2·5 g.), b. p. 84—88°/10 mm., from which 1-*acetoxyacetyl*-2-*methyl*cyclo*hexanol semicarbazone* was prepared (in pyridine solution). The derivative (0·2 g.) formed needles, m. p. 204° (decomp.) from ethanol (Found : C, 52·9; H, 7·6; N, 15·2. $C_{12}H_{21}O_4N_3$ requires C, 53·1; H, 7·7; N, 15·5%).

*Ethyl* α-*Chloro*-1-*hydroxy*-2-*methyl*cyclo*hexylacetate*.—To dry magnesium amalgam [from magnesium (24 g.) and mercury (1200 g.)] ether (1000 c.c.) was addded with vigorous stirring, followed by a portion (20 c.c.) of a mixture of 2-methyl*cyclo*hexanone (112 g.) and ethyl dichloroacetate (209 g.). Iodine (0·5 g.) was added and then the remainder of the mixture; the temperature was not allowed to exceed 15° (water cooling). After being stirred overnight, the

mixture was poured on crushed ice (500 g.) and acetic acid (250 c.c.), the solution extracted with ether (6 × 1000 c.c.), and the extract washed successively with aqueous sodium hydrogen carbonate, water (2 × 200 c.c.), and saturated aqueous sodium hydrogen sulphite (50 g. in 200 c.c.). Evaporation of the ether, fractionation of the residue through a 12″ column and redistillation of the fraction (143 g.), b. p. 100—105°/0·004 mm., gave *ethyl α-chloro-1-hydroxy-2-methylcyclohexylacetate*, b. p. 78°/0·003 mm., $n_D^{20}$ 1·4702 (Found: C, 55·9; H, 8·1; Cl, 14·8. $C_{11}H_{19}O_3Cl$ requires C, 56·2; H, 8·1; Cl, 15·1%).

*Ethyl α-1-Epoxy-2-methylcyclohexylacetate.*—The above ester (23·4 g.) in ethanol (50 c.c.) was treated dropwise with sodium ethoxide [from sodium (2·3 g.)] in ethanol (100 c.c.). The solvent was removed *in vacuo*, and extraction with ether followed by distillation of the extract gave the *epoxide*, b. p. 130°/10 mm., $n_D^{21}$ 1·4620 (Found: C, 66·9; H, 9·2. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%).

*Reduction of the α-Chloro-ester.*—The ester (23·4 g.) dissolved in ether (100 c.c.) was added dropwise to lithium aluminium hydride (3·8 g.) in ether (500 c.c.). The complex was decomposed with 5% hydrochloric acid and extracted with ether. Distillation through a 6″ column gave low-boiling liquid and a fraction, b. p. 120°/0·004 mm., which solidified at 0° and formed flat prisms (9 g.), m. p. 77—78° [from light petroleum (b. p. 60—80)], of *2-chloro-2-(1-hydroxy-2-methylcyclohexyl)ethanol* (Found: C, 56·2; H, 8·9; Cl, 18·0. $C_9H_{17}O_2Cl$ requires C, 56·0; H, 8·8; Cl, 18·4%).

*Dehydration of the α-Chloro-ester.*—To the chloro-ester (65 g.) in pyridine (66 g.) phosphorus oxychloride (42·5 g.) was added dropwise at 0° with stirring during 1 hr. After 24 hr. at room temperature and 0·5 hr. on the water-bath the solution was poured on crushed ice, made just acid (Congo red), and then extracted with ether. Distillation gave the unsaturated *α-chloro-ester* (37 g.), b. p. 81°/0·003 mm., $n_D^{18}$ 1·4810 (Found: C, 60·9; H, 8·1; Cl, 16·6. $C_{11}H_{17}O_2Cl$ requires C, 70·0; H, 7·9; Cl, 16·3%).

*Reduction of the Unsaturated Ester.*—The unsaturated ester (21·7 g.) in dry ether (100 c.c.) was added dropwise to lithium aluminium hydride (3·8 g.) in ether (500 c.c.). The chlorine-free unsaturated *alcohol* (13 g.), isolated in the usual manner, had b. p. 62°/0·0035 mm. (Found: C, 77·0; H, 11·4. $C_9H_{16}O$ requires C, 77·1; H, 11·4%).

I am indebted to Professor N. F. Maclagan for suggesting the work and for advice and encouragement. I thank Samuel P. Sadtler and Son Inc., Philadelphia, for the infra-red spectra, and Mr. D. Warren for technical assistance. I am also indebted to the Empire Rheumatism Council and the Governors' Discretionary Fund, Westminster Hospital, for financial assistance.

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## 536. *The Liquid Dinitrogen Tetroxide Solvent System. Part XV.* Thermal and Conductivity Measurements on Nitromethane–Liquid Dinitrogen Tetroxide Mixtures.*

By C. C. Addison, N. Hodge, and J. Lewis.

Liquidus and solidus curves, and electrical conductivities, have been determined for mixtures of nitromethane and liquid dinitrogen tetroxide over the full concentration range. The liquidus curves form a simple eutectic system (eutectic temperature −56°, at 53 wt.% of nitromethane), and there is no evidence of compound formation. The solidus curves indicate partial miscibility in the solid state. Dinitrogen tetroxide is a very weak electrolyte ($N_2O_4 \rightleftharpoons NO^+ + NO_3^-$) in nitromethane; the specific conductivity values pass through a broad maximum at $9·1 \times 10^{-6}$ ohm$^{-1}$ cm.$^{-1}$.

Studies of solution chemistry in liquid dinitrogen tetroxide are limited by the insolubility of many metal salts in the pure liquid. However, nitromethane gives conducting solutions of some anhydrous metal nitrates [*e.g.*, the compounds $UO_2(NO_3)_2,N_2O_4$ and $Zn(NO_3)_2,2N_2O_4$].

* Part XIV, *J.*, 1953, 1874.

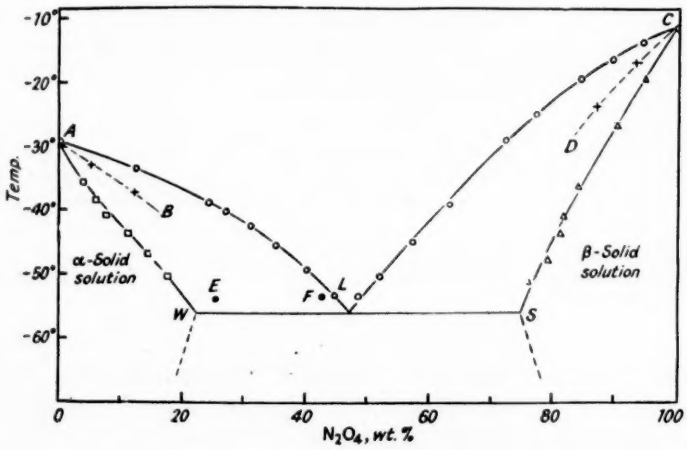
and, since nitromethane and liquid dinitrogen tetroxide are miscible in all proportions, it is of value to determine how far the properties of the tetroxide are influenced by admixture with nitromethane. The nitrosonium ion $NO^+$ is stable in nitromethane which is known to be a suitable medium for the study of reactions of ionic nitrosonium compounds such as nitrosyl perchlorate (Hantzsch and Berger, *Z. anorg. Chem.*, 1930, **190**, 321) and nitrosyl hydrogen sulphate (Hantzsch, *Z. physikal. Chem.*, 1909. **65**, 41; Angus and Leckie, *Trans. Faraday Soc.*, 1935, **31**, 958).

The very slow rate of reaction between some metals (*e.g.*, uranium) and liquid dinitrogen tetroxide is considerably accelerated by the presence of nitromethane, which has dielectric constant $\varepsilon = 37$ (Lattey and Gatty, *Phil. Mag.*, 1929, **7**, 985). Dinitrogen tetroxide ionises completely into $NO^+$ and $NO_3^-$ ions in media of very high dielectric constant; and, if the addition of nitromethane to the tetroxide causes an increase in its ionisation by increasing the dielectric constant of the medium rather than by compound formation, then reactions of the mixture with metals may be treated as identical, except in velocity, with reactions of the tetroxide alone. The physical properties reported in this paper were therefore determined in order to ascertain the nature of dinitrogen tetroxide in nitromethane solution.

## Results and Discussion

*Thermal Measurements.*—The phase diagram is shown in Fig. 1. The liquidus curves form a simple eutectic system indicating the absence of compound formation. The

Fig. 1.




eutectic temperature is −56·0°, at a composition 53·0 wt. % of nitromethane. The crystals formed when a mixture on the tetroxide side of the eutectic was cooled were granular and similar in appearance to crystals of pure dinitrogen tetroxide, and settled rapidly to the bottom of the containing vessel. The crystals formed from liquid mixtures on the nitromethane side of the eutectic were flocculent, colourless plates which settled very slowly. The solidus curves indicate partial miscibility in the solid state. Supercooling was pronounced in mixtures of all compositions; the melting points of the solid which first separated from strongly supercooled mixtures fall on curves *AB* and *CD* (Fig. 1), which are displaced from the true solidus curves (cf. $N_2O_4$–NOCl mixtures; Part II, *J.*, 1949, S218). The technique employed defined the position of the solidus curves over most of their length with sufficient accuracy, but it was difficult to obtain points on the solidus curves very near to the eutectic temperature. For example, when the minimum quantity of crystals necessary for examination was separated from liquid of composition represented by point *L* the solidus point *E* was obtained. When the crystals were melted and re-

frozen, and the melting point again determined, point *F* was obtained. The original crystal crop was therefore not homogeneous (resulting from crystallisation on both sides of the eutectic composition) but such observations were of value in confirming the existence of two distinct solid solutions. On slow crystallisation of a mixture of any composition, the stage at which the liquid passed the eutectic proportions was visually evident by a sharp change in crystal form. The miscibility limit of the β-solid solution, represented by point *S*, occurs at a molecular ratio $MeNO_2 : N_2O_4$ of 1 : 2; the unit cube of solid dinitrogen tetroxide contains twelve $NO_2$ units (Vegard, *Z. Physik*, 1931, **68**, 184). This ratio is therefore consistent with one-in-three replacement of $N_2O_4$ by $MeNO_2$ molecules. The corresponding ratio for the α-solid solution (point *W*) is about 5 : 1.

*Electrical Conductivities.*—Fig. 2 shows the electrical conductivity of nitromethane–dinitrogen tetroxide mixtures at −10°. On contact with dinitrogen tetroxide vapour the specific conductivity of nitromethane increased almost immediately from $1 \times 10^{-7}$ (for the pure liquid) to $2{\cdot}2 \times 10^{-6}$ ohm$^{-1}$ cm.$^{-1}$, although the quantity of tetroxide absorbed was minute. On addition of liquid tetroxide, the conductivity continued to rise slightly to a broad maximum at about 20 wt. % of dinitrogen tetroxide and $\kappa = 9{\cdot}1 \times 10^{-6}$ ohm$^{-1}$ cm.$^{-1}$ (cf. $3{\cdot}5 \times 10^{-4}$ ohm$^{-1}$ cm.$^{-1}$ for mixtures of the tetroxide with diethylnitrosamine, which has a similar pure liquid conductivity and dielectric constant, but forms an addition compound with the tetroxide). Thereafter, the conductivity falls gradually to the value for pure dinitrogen tetroxide ($10^{-12}$ ohm$^{-1}$ cm.$^{-1}$). There is therefore no feature in this curve to suggest compound formation in the liquid state. The initial rise in conductivity is considered to arise only from enhancement of the ionic dissociation $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ in a medium of high dielectric constant; the subsequent change in conductivity reflects the gradual decrease in dielectric constant of the mixture.

The change in conductivity of a 43 wt. % solution of dinitrogen tetroxide in nitromethane with temperature is shown in the following Table:

| Temp. | 11·2° | 1·0° | −10·0° | −12·0° | −13·0° | −14·0° | −19·2° | −31·4° | −40·0° | −50·0° |
|---|---|---|---|---|---|---|---|---|---|---|
| Specific conductivity ($10^6\kappa$, ohm$^{-1}$ cm.$^{-1}$) | 7·03 | 6·45 | 5·25 | 5·07 | 4·95 | 4·86 | 4·45 | 3·54 | 2·81 | 2·05 |

Over this temperature range, the conductivity changes linearly with temperature. The value ($8 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$/degree) and the sign of the temperature coefficient confirm that the ions present in the liquid are thermally stable.

Values for the equivalent conductivity Λ, extended to very low concentrations of dinitrogen tetroxide in nitromethane, are:

| Λ (ohm$^{-1}$) | 1·29 | 1·17 | 0·703 | 0·347 | 0·190 | 0·093 | 0·063 | 0·047 | 0·031 |
|---|---|---|---|---|---|---|---|---|---|
| Concn. of $N_2O_4$ (molar) | 0·00026 | 0·00045 | 0·00084 | 0·0022 | 0·0045 | 0·012 | 0·025 | 0·051 | 0·12 |

The magnitude of the Λ values, and their variation with concentration, indicate that even in dilute solution dinitrogen tetroxide behaves as a very weak electrolyte. Since the specific conductivity does not exceed $10^{-5}$ ohm$^{-1}$ cm.$^{-1}$, the degree of electrolytic dissociation is clearly very small, but it is considerable in comparison with that occurring in pure liquid dinitrogen tetroxide (*J.*, 1951, 1294). Because of the high electrical resistance of these mixtures, attempts to identify the ionic species were not made, but there is now no reason to suppose that the dissociation of dinitrogen tetroxide in nitromethane differs in any way (other than degree) from that in the pure tetroxide.

## Experimental

*Materials.*—Liquid dinitrogen tetroxide was prepared and purified as described in Part III (*J.*, 1951, 1289). The nitromethane was dried over calcium chloride for a week, refluxed for 12 hr. in a current of dry air to remove volatile impurities and fractionated twice through a 4-ft. column. The purity of the product was followed by incorporating a conductivity cell in the receiver at the top of the column. The receiver was fitted with a syphon so that the distillate could be collected, and its conductivity measured, in 13-ml. batches. The results below show the variation in conductivity of alternate batches during the second fractionation:

| $10^7\kappa$ (ohm$^{-1}$ cm.$^{-1}$) | 44·5 | 19·0 | 4·45 | 1·55 | 1·49 | 1·08 |
|---|---|---|---|---|---|---|
| Distillation temp. | 100·5—110·7° | 100·7—100·8° | 100·9° | 101·0° | 101·0° | 101·0° |

The conductivity of the nitromethane used for Figs. 1 and 2 was near $1 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$, but the best sample had $\kappa = 0{\cdot}45 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$. These values were increased somewhat even on pouring from one "dry" vessel into another in a closed system, so that samples were normally taken directly from the receiver syphon. Weight percentages were calculated by assuming densities 1·131 for nitromethane (Wright, Murray-Rust, and Hartley, *J.*, 1931, 199) and 1·49 for dinitrogen tetroxide.

*Phase Diagram.*—The mixtures used to obtain points on the liquidus curve were prepared by direct weighing in closed tubes, with suitable cooling. The m. p.s were determined from breaks in the warming curves. The mother-liquor was readily decanted from the granular crystals of β-solid solution; for the β-solidus curve the procedure described in Part II (*loc. cit.*) was therefore followed. Because of the flocculent nature of crystals of α-solid solution, adequate separation was not possible by decantation, and the filter-plate modification (Fig. 3) was therefore used. The minimum necessary quantity of crystals was formed by cooling about 100 ml. of liquid in vessel *A*. With very gentle suction applied through a phosphoric oxide guard tube at *B*, the assembly was tilted and the liquid filtered through a sintered-glass filter-plate *C* (size 2) into vessel *D*, which was identical with *A*. If the slight vacuum was released suddenly, the mat of crystals was displaced from plate *C*, and could be shaken into *A* for m. p. determination. The composition of the liquid in *D* was then adjusted, *A* and *D* were disconnected and joined through

FIG. 2.

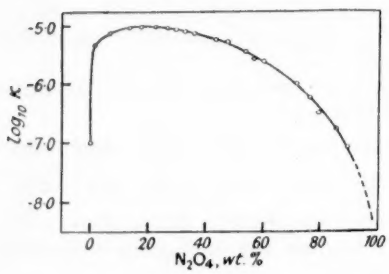
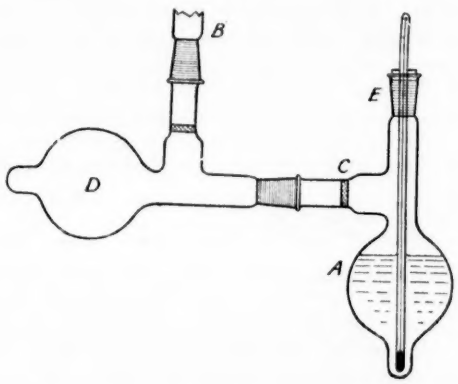



FIG. 3.




joints *B* and *E*, the composition in *D* was determined from the position of the m. p. on the known liquidus curve, and the process repeated. When points on the solidus curves which approach the eutectic temperature were being obtained, the m. p. of the solid was taken immediately after isolation, and again after refreezing; agreement confirmed the absence of contamination due to the solid solution of the opposite side of the eutectic point. The thermometer used was calibrated against the m. p. of pure mercury, chloroform, carbon tetrachloride, nitromethane, chlorobenzene, and dinitrogen tetroxide.

*Conductivity Measurements.*—A Mullard cell G.M.4221 (cell constant 2·25) was assembled as described in Part VI (*J.*, 1951, 1303, Fig. 4) and used in conjunction with a Mullard Measuring Bridge type G.M. 4140/1. Nitromethane (12 ml.) was introduced directly into the cell (capacity 19 ml.) from the top of the fractionating column. The whole cell assembly was immersed in a solid carbon dioxide–alcohol bath at −10°, and the conductivity measured. The graduated side-limb was filled with dinitrogen tetroxide (7 ml.), and the change in conductivity of the nitromethane observed as the tetroxide vapour diffused into the cell. The concentration range 0—43% of tetroxide was covered by small (0·5 ml.) additions of tetroxide from the side-limb. The range 73—100% of tetroxide was covered in a similar experiment by adding nitromethane to a cell containing dinitrogen tetroxide. Intermediate mixtures were obtained by adding nitromethane from the side-limb to a 7 : 5 (vol.) mixture of tetroxide and nitromethane in the cell.

For conductivity measurements on very dilute solutions of tetroxide, the cell consisted of a B24 glass tube into which a microburette (the tap of which was protected by silicone grease) was sealed as a side arm. The cell was fitted with a capillary tube through which liquid could

be withdrawn, and a vent-tube guarded by phosphoric oxide; 12 ml. of a 2M-solution of dinitrogen tetroxide were added to the cell. By successively adding nitromethane from the microburette, and withdrawing liquid from the cell, the conductivity of a series of concentrations down to 0·00026M was measured. Stirring after each addition was effected by rotating the electrode assembly.

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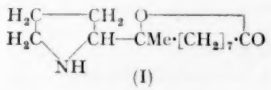
## 537. *Constitution of Carpaine.*

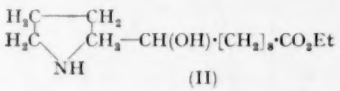
By T. R. GOVINDACHARI and N. S. NARASIMHAN.

Dehydrogenation of ethyl 10-hydroxy-10-2′-pyrrolidinyldecanoate with palladium–charcoal yielded a pyrrole and not a pyridine derivative. Dehydrogenation of ethyl carpamate yielded ethyl carpyrinate, proved to be a 3- or 5-hydroxypyridine derivative. Carpaine is therefore a piperidine alkaloid and the hydroxyl group involved in lactone formation should therefore be at position 3 or 5 of the piperidine ring.

BARGER, ROBINSON, and WORK (*J.*, 1937, 711) assigned structure (I) to the alkaloid carpaine from *Carica papaya* L. Rapaport and Baldridge (*J. Amer. Chem. Soc.*, **1951**, **73**, 343) obtained myristic acid by a two-stage Hofmann degradation of carpaine, proving conclusively that this structure was untenable. The formulation of carpaine as a pyrrolidine derivative was based on the observation (Barger, Girardet, and Robinson,



(I)



(II)

*Helv. Chim. Acta*, **1933**, **16**, 90) that carpyrine and *apo*carpyrine obtained by dehydrogenation of carpaine with selenium gave colour tests with *p*-dimethylaminobenzaldehyde normally given by pyrrole compounds. Recently, Rapaport and Baldridge (*J. Amer. Chem. Soc.*, 1952, **74**, 5365) showed that deoxycarpyrinic acid obtained by dehydrogenation of carpaine with palladium–charcoal was a pyridine derivative which could be oxidized to pyridine-2 : 6-dicarboxylic acid and that the *p*-dimethylaminobenzaldehyde test is not specific to pyrrole derivatives, being also given by 2 : 6-lutidine (and deoxycarpyrinic acid). They also sought to prove that expansion of a five-membered to a six-membered ring could not have taken place by showing that methyl 9-(5-methyl-2-pyrrolidinyl)nonanoate yielded only the corresponding pyrrole derivative under the same conditions of dehydrogenation.

Ring expansion would, however, be more likely if an α-amino-alcohol system were present in the pyrrolidine derivative. We find, however, that 10-hydroxy-10-2′-pyrrolidinyldecanoate (II), an α-amino-alcohol, gives on dehydrogenation with palladium–charcoal only a pyrrole derivative. Carpaine is therefore unlikely to be a pyrrolidine derivative.

Dehydrogenation of carpaine by palladium–charcoal leads to loss of 2 mols. of hydrogen and elimination of the hydroxylic oxygen atom involved in lactone formation, as reported by Rapaport and Baldridge (*loc. cit.*). The location of this oxygen atom is therefore left uncertain.

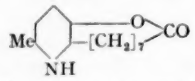
We find that ethyl carpamate on similar dehydrogenation yields three mols. of hydrogen and a product to which the name ethyl carpyrinate is assigned. Ethyl carpyrinate was soluble in dilute acids and in dilute sodium hydroxide solution, but insoluble in sodium carbonate solution. It gave a cherry-red colour with ferric chloride solution and a blue colour with the Folin–Denis reagent for phenols. Its absorption spectrum (see Figure) closely resembles that of 3-hydroxypyridine (Specker and Gawrasch, *Ber.*, 1942, **75**, 1338), and the shifts in absorption maxima in acidic and basic media are in the same direction and

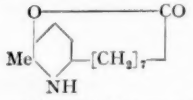
of the same order with both compounds (see Table). Ethyl carpyrinate is therefore an ethyl 8-(6-methyl-2-pyridyl)octanoate with a hydroxyl group in either the 3- or the 5-

| | Ethyl carpyrinate | | | | | 3-Hydroxypyridine * | | | |
|---|---|---|---|---|---|---|---|---|---|
| In EtOH : | $\lambda_{max.}$ | 223 | 247 | 287 | In MeOH : | $\lambda_{max.}$ | 243 | 278 | — |
| | log ε | 3·91 | 2·75 | 3·78 | | log ε | 2·68 | 3·60 | — |
| In 0·1N-HCl–EtOH : | $\lambda_{max.}$ | 234 | 251 | 302 | In 0·1N-HCl–MeOH : | $\lambda_{max.}$ | 245 | 284 | — |
| | log ε | 3·80 | 2·15 | 3·97 | | log ε | 2·22 | 3·81 | — |
| In 0·01N-KOH–EtOH : | $\lambda_{max.}$ | 247 | 272 | 310 | In 0·1N-NaOMe–MeOH : | $\lambda_{max.}$ | 238 | 265 | 304 |
| | log ε | 4·00 | 2·78 | 3·79 | | log ε | 4·00 | 2·80 | 3·63 |

* Values from Specker and Gawrasch (*loc. cit.*).

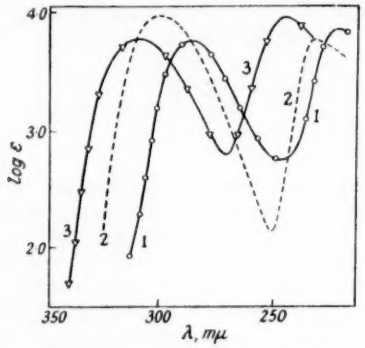
position of the ring. In carpaine, the point of attachment of the lactone ring to the piperidine nucleus should correspond, leading to structure (III) or (IV) for the alkaloid. Further experiments are in progress to distinguish between these possibilities.

(III) 

(IV)

On the basis of the above observations, carpamic acid would have a secondary hydroxyl group. We find that the diol obtained by reduction of carpaine with lithium aluminium hydride yielded a tribenzoyl derivative. Only a dibenzoate would be expected if the hydroxylic oxygen involved in lactone formation were tertiary as in (I).




*Ethyl carpyrinate* :
1, *in* EtOH,
2, *in* 0·1N-HCl–EtOH,
3, *in* 0·01N-KOH–EtOH.

## Experimental

Ultra-violet absorption spectra were determined in a Beckman Model DUV Spectrophotometer.

2-ω-*Carbethoxynonanoylpyrrole*.—This was prepared by the method of Barger, Robinson, and Short (*J.*, 1937, 715), except that the pyrrylmagnesium bromide was run straight from the flask in which it was prepared by a tap provided at the bottom into the solution of the 9-carbethoxynonanoyl chloride in ether. The yield of the product distilling at 180—210°/0·5 mm. varied between 40 and 50%. Recrystallized from light petroleum (b. p. 50—52°), it had m. p. 28°.

*Ethyl* 10-*Hydroxy*-10-2′-*pyrrolidinyldecanoate*.—A solution of the foregoing ester (0·2 g.) in acetic acid (10 ml.) was reduced at a hydrogen pressure of 60 lb./sq. in. in the presence of Adams catalyst (0·1 g.). After 2 hr., the solution was filtered. The total filtrate from several batches of ester (total 1·3 g.) was diluted with distilled water (150 ml.). The non-basic material was extracted with ether (2 × 75 ml.). The combined ethereal extracts were shaken with 30-ml. portions of water until free from basic material. The combined aqueous solutions were rendered distinctly basic with solid sodium carbonate and after saturation with potassium chloride extracted with ether (5 × 75 ml.). The ethereal extract was dried ($Na_2SO_4$) and evaporated. The semi-solid residue (0·8 g.) was recrystallised from light petroleum (b. p. 50—52°), giving the *hydroxy-ester* (0·42 g.), m. p. 69·5—70·5° (Found : C, 67·9; H, 10·8; N, 4·9. $C_{16}H_{31}O_3N$ requires C, 67·4; H, 10·9; N, 4·9%). Evaporation of the light petroleum mother-liquors yielded a basic oil, apparently stereoisomeric with the above compound.

Hydrolysis with alcoholic 0·5N-potassium hydroxide gave the corresponding amino-acid, isolated as the *hydrochloride*, m. p. 124·5—126·5° (Found: C, 57·3; H, 9·65; N, 4·5. $C_{14}H_{28}O_3NCl$ requires C, 57·5; H, 9·5; N, 4·8%).

10-*Hydroxy*-10-2′-*pyrryldecanoic Acid*.—A solution of ethyl 10-hydroxy-10-2′-pyrrolidinyldecanoate (0·5 g.) in *p*-cymene (25 ml.) was heated under reflux with 5% palladised charcoal (0·2 g.), in a slow stream of carbon dioxide. During 6·5 hr. 75 ml. (N.T.P.) of hydrogen were evolved (calc. for 2 mols., 78·6 ml.), after which evolution ceased. The solution was cooled and filtered, and the residue washed with benzene (50 ml.). The filtrate was extracted with N-acetic acid (3 × 50 ml.). Evaporation of the acid extract gave, however, no residue, showing absence of basic material in the dehydrogenation product. The benzene–*p*-cymene solution was concentrated *in vacuo* to 25 ml. and refluxed for 9 hr. after addition of alcoholic N-potassium hydroxide (50 ml.). The solvent was then removed *in vacuo* and the residue was treated with water (100 ml.). After being shaken with ether (2 × 75 ml.), the aqueous extract was rendered just acidic to Congo-red and extracted with ether (3 × 75 ml.). Removal of ether after drying ($Na_2SO_4$) yielded a brownish semi-solid mass (0·3 g.). This was purified by sublimation at 165—175°/0·5 mm., giving a colourless material, m. p. 70—74°, excessively soluble in all solvents and becoming pink rapidly. Two recrystallisations from 60% alcohol yielded a product, m. p. 76—78°, but it was not obtained analytically pure owing to the extreme ease of decomposition.

*Ethyl Carpyrinate*.—A solution of ethyl carpamate (1·0 g.) in *p*-cymene (50 ml.) was heated under reflux with 5% palladised charcoal (0·5 g.) in a current of carbon dioxide. In about 3 hr. 240 ml. (N.T.P.) of hydrogen was evolved (calc. for 3 mols., 235·8 ml.), after which evolution ceased. The solution was cooled, filtered, and washed with benzene (50 ml.). The combined filtrate and washings were thrice extracted with 2N-acetic acid (3 × 50 ml.). The acid extract was concentrated to 20 ml. and made slightly basic with solid sodium carbonate, saturated with potassium chloride, and extracted with ether repeatedly. The combined ethereal extracts were dried ($Na_2SO_4$) and evaporated, yielding a colourless crystalline solid (0·9 g.), m. p. 77—78°. Recrystallisation from absolute ether gave crystals of *ethyl carpyrinate*, m. p. 78—80° (Found: C, 68·9; H, 8·8; N, 4·9. $C_{16}H_{25}O_3N$ requires C, 68·8; H, 9·0; N, 5·0%).

Carpyrinic acid was obtained in quantitative yield by the hydrolysis of its ester with alcoholic 0·5N-potassium hydroxide and was isolated as the *hydrochloride* which, recrystallised from anhydrous acetone, had m. p. 85—86·5° after drying for 24 hr. at 80° (Found: C, 58·7; H, 7·8; N, 5·05%; *C*-Me, 0·88 group. $C_{14}H_{22}O_3NCl$ requires C, 58·4; H, 7·65; N, 4·9%). Unlike deoxycarpyrinic acid hydrochloride this is insoluble in chloroform.

*Reduction of Carpaine with Lithium Aluminium Hydride*.—A solution of carpaine (1 g.) in dry ether (50 ml.) was added dropwise to lithium aluminium hydride (2·0 g.) in ether (50 ml.). The mixture was stirred and refluxed for 4 hr. Next morning sufficient water was added to decompose the excess of hydride. The ether was decanted and the residue repeatedly extracted with ether. The combined ethereal extracts were dried ($Na_2SO_4$) and evaporated. The residue (0·97 g.; m. p. 48—52°) was dissolved in cold absolute ether, and the solution filtered and left in the ice-box overnight. The *product* separated as colourless needles, m. p. 49—52° (Found: C, 69·2; H, 11·9; N, 5·85. $C_{14}H_{29}O_2N$ requires C, 69·1; H, 11·9; N, 5·7%). Benzoylation in pyridine gave a *tribenzoyl* derivative, m. p. 76—78° (from dilute alcohol) (Found: C, 75·3; H, 7·8; N, 2·7. $C_{35}H_{41}O_5N$ requires C, 75·7; H, 7·4; N, 2·5%).

We are deeply indebted to Professor Roger Adams, University of Illinois, for arranging for the analyses. We thank Dr. B. R. Pai and Mr. R. Peter for their interest and for making available the carpaine required. We also thank the Honorary Director, Indigenous Drugs Research Committee, the Principal, College of Indian Medicine, and the Government of Madras for the award of a scholarship to one of us (N. S. N.).

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## 538. *The Anodic Behaviour of Copper in Neutral and Alkaline Chloride Solutions.*

By H. Lal and H. R. Thirsk.

The anodic behaviour of copper in neutral and alkaline sodium chloride solutions, in the presence and in the absence of oxygen, has been examined electrochemically by observing changes in the overpotential occurring during constant-current polarization and after the current has been interrupted. Particular attention has been paid to the conditions under which the metal passes freely into solution, to the nature of the oxide or salt deposited on the anode surface, and to the effect of increasing alkalinity on these phenomena. A general discussion of the experimental work has been given which, although omitting a detailed description of the results, presents an overall picture of the behaviour of the system.

Under equilibrium conditions a satisfactory description of the corrosion of a copper surface in aqueous chloride solutions over the whole pH range can be made by a theoretical study of the type described by Pourbaix ("Thermodynamics of Dilute Aqueous Solutions," Arnold, London, 1949). This theoretical approach considerably extends the treatment of such systems described some years previously by Gatty and Spooner ("The Electrode Potential Behaviour of Corroding Metals in Aqueous Solution," Oxford, Clarendon Press, 1938), Krueger and Kahlenberg (*Trans. Electrochem. Soc.*, 1930, **58**, 341), and Schmidt and Winkelman (*Helv. Chim. Acta*, 1930, **13**, 304). Thus, by making suitable assumptions concerning the solubility products of cuprous and cupric oxides and limiting assumptions concerning the number and type of complex anions in solution, the nature of the oxide or salt predominating on the copper surface can be calculated. Furthermore, changes in the equilibrium brought about when the electrode potential of the copper is altered by polarization may be deduced by reference to the calculated equilibrium diagrams. It is clear, however, that the kinetics of these changes and the phenomena occurring during the forced dissolution of the metal by the passing of a current are necessarily only accessible by direct experiment.

Hedges (*J.*, 1926, 1533; 1929, 1028) carried out an extensive investigation of the kinetics of the anodic behaviour of copper in hydrochloric acid solutions when polarized by the passage of fairly large currents; he was particularly interested in certain periodic fluctuations of current and voltage which were thus produced and which he related to a periodic change in structure of the layer covering the electrode. Also, Hickling and Taylor (*Trans. Faraday Soc.*, 1948, **44**, 262) studied the behaviour of copper in alkaline solutions.

The present paper is an account of work on the Cu–$H_2O$–Cl system under neutral and alkaline conditions. Our interest has been centred on the factors controlling the free dissolution of the copper as cuprous ion or cuprous ion complex in neutral salt solutions and the maintaining of this process in alkaline solutions. Some observations have been made on periodic phenomena occurring at higher current densities. The results are discussed in two sections dealing (*A*) with neutral chloride solutions, and (*B*) with the modifications in behaviour brought about by addition of sodium hydroxide to the system.

The same experimental procedure was followed in neutral and alkaline solutions. Copper electrodes were formed from electrolytically pure wire 0·12 cm. in diameter. Areas were left exposed varying from 0·2 to 2 sq. cm., the remainder of the electrode being stopped off by coating with two layers of polystyrene, a process found satisfactory at the lower temperatures, or at higher temperatures by using a commercial thermal-setting plastic, applied in several coats, each cured at 140° for 30 min.

The electrodes were mounted by supporting them in glass tubes of $\frac{1}{4}$" internal diameter by means of small corks. The exposed metal surface was prepared by two slightly different methods. In the first a preliminary treatment with metal polish on a pad of cotton wool was followed by polishing with magnesium oxide on Selvyt cloth and a final cleaning with alcohol

and distilled water. In the second the same procedure was carried out followed by a slight etch in dilute nitric acid. Electrodes thus prepared are referred to as " polished " and " etched " electrodes respectively. The apparent area of the exposed portion was measured by means of a travelling microscope. Current densities quoted refer to the current passed divided by the measured electrode area in cm.$^2$. Solutions were made from " AnalaR " reagents.

*The Cells.*—The majority of the experiments were performed in a wide-necked bottle of about 400-c.c. capacity fitted with a Perspex lid. The electrode under examination was fixed by means of a plastic-covered clip at one end of a slot machined in the lid. A vertical wide-bore limb of a tube joined to a Luggin capillary could be advanced along the slot by means of a screw of medium pitch working in a bolt to which the limb was attached. The tip of the capillary was thus brought with accuracy adjacent to the working electrode. The other end of the vertical limb was bent round to form a U tube with a three-way tap in the top portion. The liquid junction with a saturated calomel electrode, used as a reference half-cell, was made at

FIG. 1.

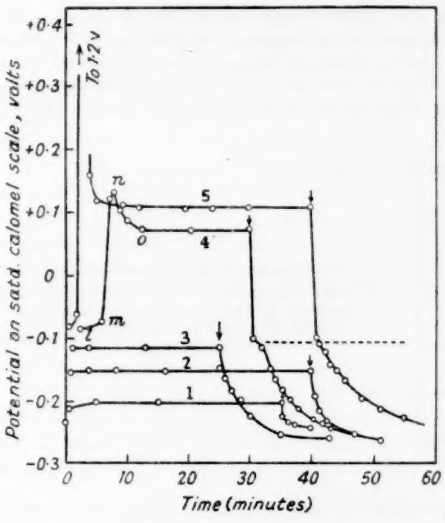


FIG. 2.

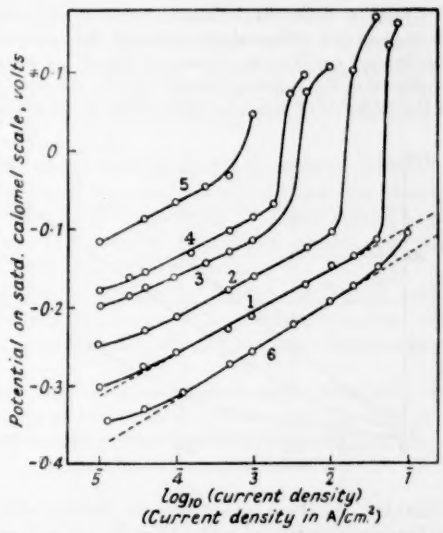


FIG. 1. *Anodic polarization curves for copper in* M-NaCl *together with curves showing the change of potential on stopping the current at the point indicated by the vertical arrow :* (1) $1 \times 10^{-5}$; (2) $1 \times 10^{-4}$; (3) $1 \times 10^{-3}$; (4) $5 \times 10^{-3}$; (5) $1 \times 10^{-2}$ A/cm.$^2$. Dotted horizontal line represents the Cu–CuCl potential.

FIG. 2. *Curves showing the relationship between potential and log (current density) for copper in sodium chloride :* (1) 4M-NaCl; (2) 2·0M-NaCl; (3) 1·0M-NaCl; (4) 0·5M-NaCl; (5) 0·1M-NaCl; (6) 4M-NaCl. *Curves* 1—5 *at* 18°, *curve* 6 *at* 60°.

the three-way tap. A second U tube was inserted through the lid of the cell and communicated with a separate vessel containing a large platinum cathode. The cell was mounted in a thermostat which could be operated at temperatures up to 60° ± 0·1°.

In experiments for which it was decided to exclude air, a cell was used with the Perspex lid replaced by a rubber bung with extra tubes for bubbling hydrogen or nitrogen through the solution and without the facilities for the lateral movement of the Luggin capillary.

The means of obtaining a constant current supply and of measuring the overvoltage was similar to that described by Lal, Thirsk, and Wynne-Jones (*Trans. Faraday Soc.*, 1951, **47**, 70).

## *Section A.*

*Experiments in Neutral Sodium Chloride Solutions.*—A range of current densities from $10^{-5}$ to 0·1 A/cm.$^2$ were employed in 0·1, 0·5, 1·0, 2·0, and 4·0M-sodium chloride. Experiments were carried out at 17°, 40°, and 60°. A limited series of runs were made at current densities of the order of 15—80 mA/cm.$^2$.

Fig. 1 gives some typical results, showing the relation between overpotential and time to

illustrate the behaviour of the system. The graphs refer to a solution of 1M-sodium chloride at 17°, curves 1, 2, 3, 4, and 5 corresponding to values of the current densities of $0{\cdot}9 \times 10^{-5}$, $1{\cdot}0 \times 10^{-4}$, $1{\cdot}0 \times 10^{-3}$, $5{\cdot}0 \times 10^{-3}$ and $1{\cdot}0 \times 10^{-2}$ A/cm.². The arrow on the right-hand side of the curves shows the point at which the polarising current was interrupted, and the subsequent curve represents the behaviour of the electrode under self-discharge. It will be noted that curves 4 and 5 show an arrest near the $Cu$–$CuCl_2$ reversible potential, the calculated value being represented by the dotted horizontal line.

Very similar results were obtained at the different concentrations, with the lower range of current densities and at all temperatures noted above, except that in 0·1M-sodium chloride all curves rose steadily to a maximum without showing the peak value and subsequent fall as exhibited, *e.g.*, by curve 4, with a maximum at *n* and a fall to 0. In all the solutions other than 0·1M-sodium chloride the overvoltage oscillated round 1·2—1·5 volts for a few minutes when a polarising current density greater than about $1{\cdot}0 \times 10^{-2}$ A/cm.² was passed. This was a temporary phenomenon and the potential soon fell to a steady value. No evolution of oxygen was observed at the electrode.

Quite a different behaviour was noted with the higher range of current densities. At 25 mA/cm.² in 1·0M-sodium chloride the overpotential rose in 10 min. to a value of 18 v and a continuous oscillation ensued of about 1 v amplitude. Even in this case we did not observe production of oxygen at the electrode. A similar phenomenon was found with current densities of the order of 60 mA/cm.² and above in 2M-sodium chloride and above 80 mA/cm.² in 4M-sodium

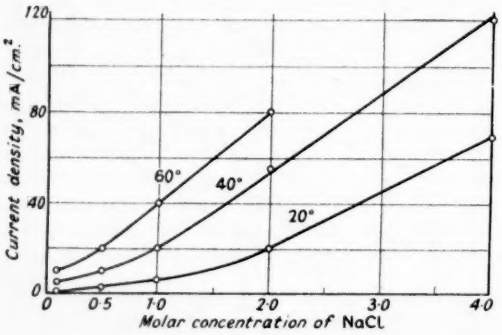


FIG. 3. *The effect of chloride concentration and temperature on the lowest current density at which cuprous chloride is deposited as a film on the electrode surface. (Unstirred solutions.)*

chloride. At these higher current densities the potential showed no tendency to fall to a steady value as with curves 4 and 5 (Fig. 1).

It was realised that when a certain current density was exceeded, dependent on the concentration of the electrolyte and the temperature, a precipitate would be formed on the electrode although the nature of the salt had to be determined. This was done by a consideration of the position of the arrests on the potential–time curves obtained after stopping the polarizing current and by some *X*-ray investigations. In the neutral chloride solutions the precipitate was shown to be cuprous chloride.

The plot of log (current density) against potential gave an almost linear relation up to a critical value of the current density corresponding to the formation of the insoluble deposits. To illustrate this, in Fig. 2 values of $\log_{10}$ (current density) are plotted against overvoltage for five different concentrations of sodium chloride at 17° (curves 1—5) and for 4M-sodium chloride at 60° (curve 6). Similar plots were obtained at 40° and 60°, and the values of the slopes have enabled us to reach some conclusions concerning the cause of the overvoltage during this stage of the dissolution of the metal. Fig. 3 shows the dependence on temperature and chloride concentration of the critical current density at which a deposit is formed on the electrode.

By repeating a selection of the above experiments in the absence of oxygen it was shown that the results in neutral sodium chloride were unaffected by the presence of air above the solution within the experimental accuracy of our potential measurements.

*Discussion.*—The equilibrium between cuprous and cupric ions in aqueous solution and a copper surface according to Fenwick (*J. Amer. Chem. Soc.*, 1926, **48**, 860) is given by

$$Cu^{++} + Cu = 2Cu^{+}; \; K = 1{\cdot}0 \times 10^{-6}$$

favouring the formation of cupric ions. This equilibrium is, however, shifted to the right by the tendency of the cuprous ions to form complexes in chloride solutions (see, *e.g.*, Noyes and Chow, *ibid.*, 1918, **40**, 739; Naray-Szabó and Szabó, *Z. phys. Chem.*, 1933, **166**, *A*, 228), with the result that copper goes into solution mainly as cuprous ions. The electrode potential at a given current density is controlled by the cuprous-ion concentration adjacent to the electrode. This concentration is determined by the difference between the rate of formation of cuprous ions, given initially by the current density and the rate of diffusion of cuprous ions away from the electrode to the bulk of the solution by means of the soluble chloride-ion complex. A dynamic equilibrium is thus established controlling the cuprous-ion concentration at the electrode surface.

The overvoltage, $\eta$, which is established along the linear portion of the curves in Fig. 2 may be reduced by stirring. This furnishes evidence that the rise in overpotential over this region is due to concentration polarization. This is not in contradiction to the linear $\eta$–log (C.D.) plot although such a relationship is commonly only associated with an activation overpotential. For example, Agar and Bowden (*Proc. Roy. Soc.*, 1938, *A*, **169**, 206) showed that, during electro-solution with the concentration of ions increasing with increasing current density and where the overpotential is determined by concentration changes of only one of the reacting ions, the linear relation $\eta = (\boldsymbol{R}T/n\boldsymbol{F}) \log (-I/I_0)$ holds providing $I$, the measured current density, exceeds a certain minimal value; $I_0$ is some limiting value of the current density and in this case $n = 1$.

The estimated value of the slope of the curve given by this simple treatment is 0·058 and 0·066 at 17° and 60°, respectively; the experimental values derived from the linear portion of curves 1—6 (Fig. 3) are $0{\cdot}05_5$ and 0·06 v at 17° and at 60°. These values are much of the same order as the calculated slopes and provide additional evidence for a diffusion-controlled overpotential rather than an activation overpotential.

The points at which cuprous chloride is precipitated are easily observed in Fig. 2 and in Fig. 1. In the latter the conditions are shown by the rapidly reached maxima of curves 4 and 5 (*e.g.*, the portion *lmno* of curve 4). In Fig. 2, a sharply rising overpotential is immediately noted.

For each salt concentration and temperature this sharp change of slope occurs at a reproducible current density, and the relation between the three factors is shown in Fig. 3. Since conditions for exceeding the copper chloride solubility product clearly depend on the temperature, the equilibrium constants for the reactions

$$CuCl + Cl^- \rightleftharpoons CuCl_2^- \text{ and } CuCl + 2Cl^- \rightleftharpoons CuCl_3^{--}$$

and the rate of production of copper ions controlled by the current density, the smooth nature of these curves is not of itself surprising. Fig. 3 is of importance, however, for the discussion of our results on the behaviour of the metal in alkaline solutions since we found difficulty in obtaining a free dissolution of the copper unless the current density over the area of attack was of the order associated in Fig. 3 with each particular temperature and chloride-ion concentration.

It has been shown by many different workers that the stable film in contact with air is cuprous oxide, and Evans (*J.*, 1925, **127**, 2484), Haase (*Chem. Fabr.*, 1934, **7**, 329; *Z. Metallk.*, 1934, **26**, 185), and Bengough *et al.* (*J. Inst. Metals*, 1913, **10**, 13; 1916, **15**, 37; 1919, **21**, 37; 1920, **23**, 97; 1924, **32**, 108) have shown that a similar film in general is formed in aqueous solution. Tourky and El Wakkad (*J.*, 1948, 750), studying the behaviour of copper electrodes in buffer solutions of varying pH and free initially from copper ions, showed that between pH 4·65 and 8·08 the electrode behaves as a well-defined metal oxide electrode. It might be expected, therefore, that the electrodes would attain initially, on open circuit, a potential independent of chloride-ion concentrations. This was not found in practice; some results are shown in the Table on p. 2643, but they agree closely with those obtained in potassium chloride solution by Gatty and Spooner (*loc. cit.*). These authors suggest that the chlorine ions when present in high concentrations cause dissolution of the oxide layer and that the electrode behaves as it would in hydrochloric acid solutions. Reduction of the chloride ion in the salt solution causes the potential to converge to a value corresponding to the presence of a $Cu_2O$ layer. Reference to Pourbaix's

discussion (*loc. cit.*) on the system shows quite clearly how the $Cu_2O$ domain is reduced on the addition of chloride ion.

The periodic oscillations at high current densities have been attributed by Hedges (*loc. cit.*) to the formation of a highly resistant oxide film on the electrode. The discontinuity necessary for periodicity was supposed to be provided by the transformation of the stable oxide film into a less resistant variety which is attacked by the electrolyte to form cuprous chloride and then washed away. Hedges's experimental observations of colour changes during the polarization were similar to those recorded by Wilman (*Discuss. Faraday Soc.*, 1947, No. 1, 252), *viz.*, through dark grey, white, light grey, to yellowish-brown. In view of Wilman's observation that at all these stages the electron-diffraction pattern showed only cuprous chloride together with some copper in the early stages of the polarization, it cannot be certain that Hedges's assumption was correct that a particular colour was an indication of the presence of an oxide film. Alternatively, the periodic phenomenon may be due to a compact cuprous chloride film, the discontinuity being provided by cupric ions formed when the chloride deposit reaches a critical thickness. These ions may disrupt or modify the film of cuprous chloride, but at the same time, since the film is also being dissolved away by the electrolyte at the cuprous chloride–solution interface, the film is reduced in thickness and a return to the condition when the electrode dissolves once again as a cuprous ion is brought about; this cycle on being repeated gives rise to the periodic phenomenon. Under these conditions glancing incidence electron diffraction would only provide evidence for the presence of cuprous chloride unless the adhering layer can be stripped off and examined at the metal–salt interface.

*Section B.*

*Experiments in Alkaline Sodium Chloride Solutions.*—The effect of making the electrolyte alkaline increased considerably the complexity of the phenomena. They were affected both by the method of preparation of the electrode and by the presence of oxygen in the electrolyte. We limit our account to the range of our experimental conditions and the features of the behaviour for which a general discussion may be given, rather than treat in detail the large variety of overpotential–current density curves obtained.

The results are separated into two groups depending on whether the solutions were in equilibrium (*a*) with oxygen at the partial pressure of the atmosphere or (*b*) with hydrogen.

(a) *Air-saturated solutions.* Solutions used were N, 2N, and 4N with respect to sodium chloride and the pH was changed by the addition of "AnalaR" sodium hydroxide. Addition of 1 g./l. led to measured pH values of 11·79, 11·41, and 11·10, respectively. Experiments were carried out at 18°, 40°, and 60°.

The steady electrode potential reached on open circuit in all solutions before polarization was about −0·15 v. Similar observations on hydrogen- and oxygen-saturated solutions have been made by other workers. Krueger and Kahlenberg (*loc. cit.*) found that in oxygen-saturated N-potassium hydroxide the open-circuit potential was much more positive than in hydrogen-saturated solutions, the values with respect to a saturated calomel electrode being −0·285 and −0·548 v, respectively, and a similar behaviour in alkaline sulphate solution was observed by Gatty and Spooner (*loc. cit.*). In more recent work by Hickling and Taylor (*loc. cit.*) it was suggested that a film of cuprous oxide was first formed on the copper electrode and this was followed by cupric oxide. The $Cu_2O$–CuO potential in an electrolyte of pH 11 should be about −0·14 v on the saturated calomel scale. This agrees well with the steady potentials we observed before polarization.

Overpotential–time curves were taken over a range of current densities of $1 \times 10^{-5}$ to $15 \times 10^{-2}$ A/cm.$^2$. As an example, the behaviour at the lower current densities is described for 4M-sodium chloride containing 1 g. of sodium hydroxide/l. at $3{\cdot}3 \times 10^{-5}$ A/cm.$^2$ and at $5 \times 10^{-3}$ A/cm.$^2$ and shown in Fig. 4(*a*) and 4(*b*). On closing of the circuit, at the lower current density, the potential first rises through a few tenths of a volt and then falls to a value, slightly positive to the Cu–CuCl reversible potential, which remains fairly steady. When the circuit is opened, the potential first shows an arrest near the Cu–CuCl potential and then continues to fall before finally rising, in a matter of hours, to the initial open-circuit potential. The extent of this fall of potential depends on the area of attack of the electrode. This area, at $3{\cdot}3 \times 10^{-5}$ A/cm.$^2$, was confined to one single red spot, the remainder of the electrode being covered with an adherent grey film. Attack quite clearly was only proceeding at one point,

the cuprous chloride formed being converted immediately into the lower oxide. As the current density was increased, the number of points of attack also increased until eventually some change was observed in the shape of the overvoltage curves in that a much more positive value was reached. This is shown by Fig. 4(*b*); the shape resembles that of curve 4 in Fig. 1, but for neutral 4N-sodium chloride in order to obtain an overvoltage curve of this type a current density of 60 mA/cm.$^2$ is required. A rough calculation concerning the relative areas attacked in the neutral and alkaline solutions shows that the current densities at the attacked areas are approximately the same in both cases. In the experiment relevant to Fig. 4(*b*) the area attacked was already quite large, and the short arrest at the Cu–CuCl potential on cessation of polarization was followed by a long arrest near the much lower $Cu_2O$–Cu potential.

Increase in pH produced a displacement of the behaviour in the sense that higher current densities were necessary in order to complete attack on the surface; decrease of pH

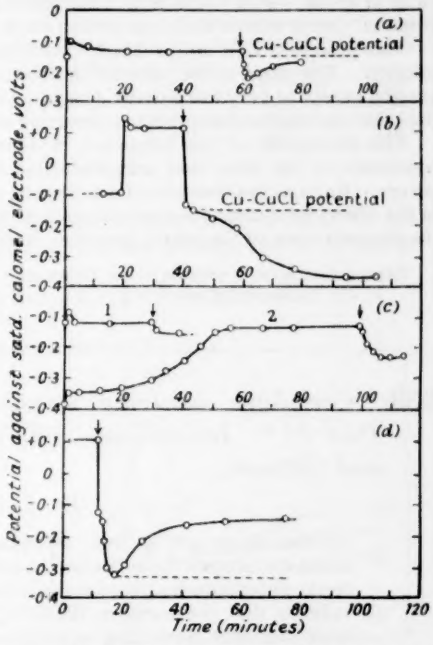


FIG. 4. *Vertical arrows show the point at which the polarizing current was switched off. Curves showing important features in the behaviour of anodically polarized copper in alkaline sodium chloride solutions: (a)* 4N-NaCl *with* 1 *g. of* NaOH/*l.*; *C.D.* $3{\cdot}3 \times 10^{-5}$ A/*cm.*$^2$. *(b) Solution as for (a); C.D.* $5 \times 10^{-3}$ A/*cm.*$^2$. *(c) Solution as for (a): curve* (1) *polished electrode, curve* (2) *etched electrode. (d) Self-discharge curve after polarization in* 2N-NaCl *with* 1 *g. of* NaOH/*l. at* $1 \times 10^{-2}$ A/*cm.*$^2$.

gave solutions in which the electrode reacted in a manner increasingly similar to that in neutral solutions; *i.e.*, complete attack occurred at lower current densites with a decreasing tendency for the formation of the protective grey film and therefore the reappearance of much more negative prepolarization potentials.

(b) *Hydrogen-saturated solutions.* Marked differences were observed with these solutions in the behaviour before and after polarization, but in general terms they can be explained fairly simply.

The polished electrodes showed an initial potential of about −0·15 v independent of chloride-ion concentration; the etched electrodes remained fairly steady at potentials near those found in neutral solutions. This is shown in the table.

*Steady potential of etched copper electrodes in neutral and hydrogen-saturated alkaline sodium chloride solutions.*

| | Neutral sodium chloride: | | Alkaline sodium chloride (1 g. NaOH/l.) | |
|---|---|---|---|---|
| | 4M-NaCl | M-NaCl | 4M-NaCl | M-NaCl |
| Potential (v) on the saturated calomel scale | −0·33 | −0·23 | −0·34 to −0·37 | −0·24 to −0·26 |

It was considered that this difference was due to the presence of a protecting oxide in the case of the polished electrode, and that the etched electrode, in the absence of such a layer, was attacked by chloride ion with subsequent formation of cuprous oxide.

On polarization of these electrodes at similar current densities, the etched electrodes fairly soon reached an overpotential comparable with that given for the polished electrodes, and subsequently the behaviour was the same. This is illustrated in Fig. 4(*c*), curves (1) and (2), again for 4N-sodium chloride with 1 g. of sodium hydroxide/l.; (1) is for the polished and (2) for the etched electrode at a current density of $10^{-5}$ A/cm.$^2$. The short vertical arrows show the point at which the polarizing current was stopped. At these low current densities the final potential lies near the CuO–$Cu_2O$ potential.

At higher current densities, as in the aerated solutions, the protective layer is destroyed and the effect is shown in Fig. 4(*d*). These results were obtained in 2N-sodium chloride with 1 g. of hydroxide/l. at a current density of $1 \times 10^{-2}$ A/cm.$^2$. The potential rose rapidly and a considerable area of the electrode showed the presence of red copper oxide. When the current was cut off, the potential fell to a short arrest at the Cu–CuCl potential and then to a steady value at about −0·34 V (the broken horizontal portion). If air was admitted to the solution the potential slowly rose to the steady value for a passivated electrode in the presence of oxygen.

This process is slow and is clearly controlled by the rate of diffusion of oxygen through the solution. The effect of the presence or absence of oxygen during the actual polarization is not marked except at very low current densities, since the diffusion of the gas is slow compared with the other electrochemical processes occurring at the electrode face.

The description of the behaviour in alkaline sodium chloride solutions does not include comments on the sharp and unreproducible fluctuations often observed in the over-potential curves. From a consideration of our data we ascribe these variations to mechanical breakdown in the otherwise continuous areas of oxide or salt on the electrode, so that they are secondary to the general course of the anodic processes described above which are themselves reproducible.

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## 539. *Complexes involving Tervalent Iron and Orthophosphoric Acid. Part II.* Ion-exchange Studies of Solutions containing Phosphate and Chloride.*

By J. E. Salmon.

The adsorption of iron, phosphate, and chloride by both cation- and anion-exchangers from ferric chloride–phosphoric acid solutions and from ferric phosphate–hydrochloric acid solutions has been studied. The results indicate that the complex, $[FeHPO_4]^+$, is adsorbed by the cation-exchanger from solutions containing equimolecular, or nearly equimolecular, amounts of ferric chloride and phosphoric acid, while the anion-exchanger adsorbs only chloride from such solutions.

Addition of hydrochloric acid to ferric phosphate solutions decreases the adsorption of iron and phosphate by the anion-exchanger. Although adsorption of chloride is simultaneously increased the iron is adsorbed as a ferric phosphate complex rather than as a chloroferriphosphate complex. The similarity of the results obtained when nitrate was substituted for chloride also suggests the absence of chloro-complexes. Only with solutions containing much chloride (Fe 0·1M, Cl 2·86M) was any evidence of such complexes obtained.

The evidence for the existence of ferric phosphate complexes and the views of previous workers were summarised in Part I,* where it was shown that in pure phosphate solutions the complex, $[Fe(PO_4)_3]^{6-}$ or $[Fe(HPO_4)_3]^{3-}$, is probably present. Since several of the complexes previously described, namely $[Fe(HPO_4)_2]^-$, $[FeH_2PO_4]^{++}$, and $[Fe(PO_4)Cl_3]^{3-}$, were reported to be formed in solutions containing chloride, the investigation has now been extended to include such solutions. As before, Amberlite I.R.A.-400 (in chloride or phosphate form) and Zeo-Karb 225 (in hydrogen form) were used.

* Part I, *J.*, 1952, 2316.

## Results

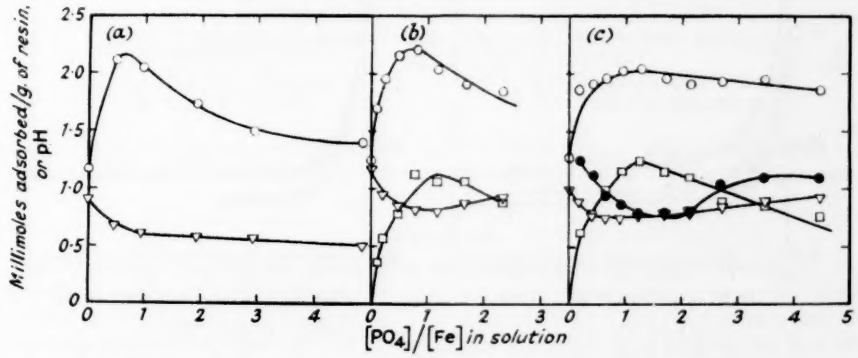
*Experiments with Ferric Chloride–Phosphoric Acid Solutions.*—The adsorption of ions from mixed solutions of ferric chloride (0·1M; pH 1·0—1·8) and phosphoric acid by both exchangers has been studied. With the anion-exchanger in the chloride form (Table 1*a*) little or no iron or phosphate was adsorbed until the ratio of phosphoric acid to iron in the solution was about 10 : 1. With a high chloride-ion concentration (2·86M) there was limited adsorption of iron and phosphate in approximately equimolecular amounts (Table 1*b*).

TABLE. 1. *Adsorption of iron, phosphate, and chloride by* I.R.A.-400-Cl.

| Solution [$PO_4$]/[Fe] | Resin, millimole adsorbed/g. of resin Fe | $PO_4$ | Cl | Solution [$PO_4$]/[Fe] | Resin, millimole adsorbed/g. of resin Fe | $PO_4$ | Cl |
|---|---|---|---|---|---|---|---|
| (*a*) *Resin* 1·000 *g.*; $FeCl_3$ (pH 1·02) 50 *ml.*; 4·85M-$H_3PO_4$. | | | | (*b*) *Resin* 3·00 *g.*; 25 *ml. of solutions* 0·1M *in* Fe *and* 2·86M *in* Cl, *but containing varying amounts* (0·1—0·585M) *of* $PO_4^{3-}$. | | | |
| 0·00 | 0·01 | Nil | 2·17 | 1·00 | 0·14 | 0·07 | 2·24 |
| 0·50 | — | ,, | 2·25 | 1·97 | 0·16 | 0·14 | 2·22 |
| 0·97 | 0·02 | ,, | 2·11 | 2·94 | 0·18 | 0·19 | 2·16 |
| 1·95 | 0·02 | ,, | 2·05 | 5·85 | 0·16 | 0·23 | 2·06 |
| 2·93 | 0·02 | ,, | 2·05 | | | | |
| 4·85 | 0·02 | ,, | 2·12 | | | | |
| 9·75 | 0·04 | 0·17 | 1·85 | | | | |

Although addition of phosphoric acid to ferric chloride solution caused a fall in the pH of the solutions in equilibrium with the cation-exchanger, this was accompanied by an increased

FIG. 1. *Adsorption of iron and phosphate from* $FeCl_3$–$H_3PO_4$ *solutions by Zeo-Karb* 225-H (0·500 g.).




(*a*) 0·1M-$FeCl_3$ (pH 1·02) + 4·85M-$H_3PO_4$; 50 ml.
(*b*) 0·1M-$FeCl_3$ (pH 1·76) + 0·25M-$H_3PO_4$; 25 ml.
(*c*) 0·1M-$FeCl_3$ (pH 1·24) + 0·3M-$H_3PO_4$; 50 ml.
○ Total Fe adsorbed. ● Fe adsorbed as $Fe^{3+}$. □ Total $PO_4$ adsorbed. ▽ pH of solution (filtrate)

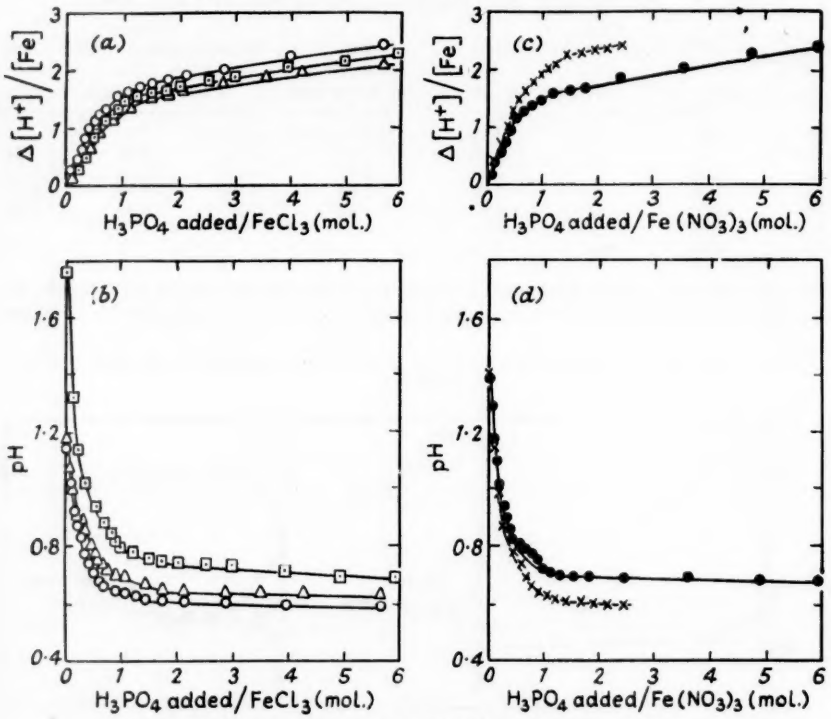
adsorption of iron, which rose to a maximum for a ratio of phosphoric acid to iron in the original solution of nearly 1 : 1 (Fig. 1*a*). There was simultaneous adsorption of phosphate, which likewise passed through a maximum (Figs. 1*b* and *c*).

pH-*Titration of Ferric Chloride Solutions with Phosphoric Acid.*—pH-Titrations with a glass electrode–saturated calomel electrode system showed that addition of phosphoric acid caused a rapid fall in pH up to a mol. ratio of 1 : 1, but thereafter the pH remained practically constant even in the presence of a considerable excess of phosphoric acid (Fig. 2*b*). Addition of an inert electrolyte, such as sodium nitrate, had no effect on the course of the titration. When sodium dihydrogen phosphate was substituted for phosphoric acid the pH passed through a minimum at a mol. ratio of 1 : 1, the decrease in pH even at the minimum being, however, markedly less than with phosphoric acid.

*Mixed Ferric Phosphate–Hydrochloric Acid Solutions.*—The effect of addition of chloride to ferric phosphate solutions has been investigated. A difficulty was the very low solubility of

ferric phosphate in dilute phosphoric acid. For anion-exchange studies it was preferable to keep the total phosphate concentration as low as possible and the solution used was 0·1M in iron and 1·5M in phosphoric acid. Although this would be in a state of metastable equilibrium at 25° (Jameson and Salmon, unpublished work) there was no precipitate of ferric phosphate after many months at room temperature. Since no adsorption of phosphate by the cation-exchanger was found with this solution (Table 2), it may be presumed that no precipitation occurred in the presence of resins either.

FIG. 2. pH *Titration of ferric chloride and nitrate with phosphoric acid.*




○ 0·1M-$FeCl_3$ (pH 1·19) + 40 g. of $NaNO_3$ per l.; 1·77M-$H_3PO_4$.
□ 0·1M-$FeCl_3$ (pH 1·76); 2·43M-$H_3PO_4$.
△ 0·1M-$FeCl_3$ (pH 1·19); 1·77M-$H_3PO_4$.
● 0·1M-$Fe(NO_3)_3$; 1·49M-$H_3PO_4$.
× 0·1M-$Fe(NO_3)_3$ + 40 g. of NaCl per l.; 1·49M-$H_3PO_4$.

The adsorption of ions from this solution and from mixtures of it with 0·3M-hydrochloric acid by both exchangers has been studied. With the cation-exchanger (Table 2) iron was adsorbed to some extent, but less than from ferric chloride solutions of the same pH where

TABLE 2. *Adsorption of iron, phosphate, and chloride by Zeo-Karb* 225-H (0·500 *g.*) *from* 50 *ml. of a mixture of ferric phosphate solution* ([*Fe*] 0·1M, [$PO_4$] 1·5M) *and* 0·3M-*hydrochloric acid.*

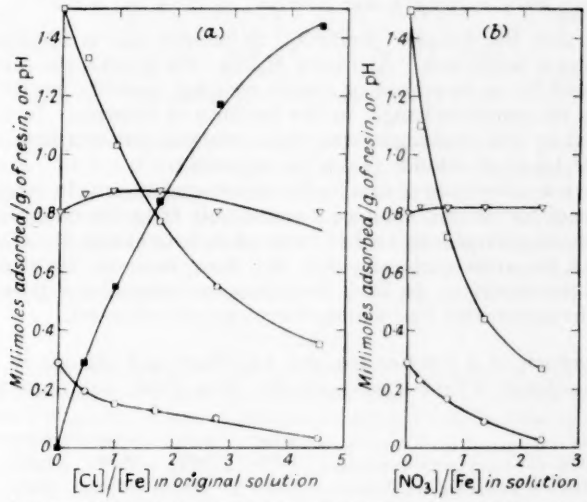
| Solution | | Resin, millimole adsorbed/g. of resin | | Solution | | Resin, millimole adsorbed/g. of resin | |
|---|---|---|---|---|---|---|---|
| [Cl]/[Fe] | pH * | Fe | $PO_4$ | [Cl]/[Fe] | pH * | Fe | $PO_4$ |
| 0·00 | 0·75 | 0·55 | Nil | 1·71 | 0·78 | 0·67 | Nil |
| 0·41 | 0·79 | 0·58 | ,, | 2·79 | 0·76 | 0·64 | 0·04 |
| 0·96 | 0·78 | 0·67 | ,, | 4·53 | 0·74 | 0·70 | 0·06 |

* Of solution in equilibrium with the resin.

1·1—1·2 millimoles of iron are adsorbed per g. of resin. Phosphate was adsorbed only at high ratios of chloride to iron in the solutions, and chloride apparently not at all.

With the anion-exchanger both iron and phosphate were adsorbed from the ferric phosphate

FIG. 3. *Adsorption from* $Fe(H_2PO_4)_3$–HCl *and* $Fe(H_2PO_4)_3$–$HNO_3$ *solutions by* I.R.A. 400–$PO_4$ (1·000 g.).




(*a*) $Fe(H_2PO_4)_3$ solution, [Fe] 0·1M, [$PO_4$] 1·5M; HCl, 0·30M; 50 ml.
(*b*) $Fe(H_2PO_4)_3$ solution as in (*a*); $HNO_3$, 0·32M; 50 ml.

○ Total Fe adsorbed. □ Total $PO_4$ adsorbed.
■ Total Cl adsorbed. ▽ pH of solution (filtrate).

solution alone (in agreement with previous work, Part I), but as chloride was added to the solution this was readily adsorbed by the resin at the expense of both the iron and the phosphate (Fig. 3*a*).

## DISCUSSION

The experiments with the ferric chloride–phosphoric acid solutions indicate that in them the complex present in major proportion must be a cationic complex, such as $[FeHPO_4]^+$ or $[FeH_2PO_4]^{++}$, since both the ion-exchange and the pH-titration data seem to confirm previous reports of a complex containing one phosphate group per iron atom. It seems unlikely that the chloroferriphosphate anionic complexes are formed unless they are weakly ionised—which is not in accord with conductivity data reported by Dede (*Z. anorg. Chem.*, 1922, **125**, 28) and Ricca and Meduri (*Gazzetta*, 1934, **64**, 235). The marked increase in conductivity found by these workers and attributed by them to the formation of a strong acid, $H_3[Fe(PO_4)Cl_3]$, appears to be due to the liberation of hydrochloric acid according to eqns. (1) or (2):

$$FeCl_3 + H_3PO_4 \rightleftharpoons [FeH_2PO_4]^{++} + H^+ + 3Cl^- \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(cf. Jensen, *Z. anorg. Chem.*, 1934, **221**, 1)

$$FeCl_3 + H_3PO_4 \rightleftharpoons [FeHPO_4]^+ + 2H^+ + 3Cl^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(cf. Lanford and Kiehl, *J. Amer. Chem. Soc.*, 1942, **64**, 291).

If the iron present as such a complex is subtracted from the total iron adsorbed, it is found that the amount of ferric ions, $Fe^{+++}$, adsorbed does fall with the pH of the solution as would be expected (Fig. 1*c*). The assumption of adsorption of the complex, $[FeH_2PO_4]^{++}$, together with ferric ions leads to a high value for the capacity of the resin (4·6—5·0 milliequiv./g.) while the assumption that $[FeHPO_4]^+$ is adsorbed leads to a more reasonable value (3·6—4·2 milliequiv./g.; capacity found 3·75 milliequiv./g.). Further, the results

of the pH titrations when interpreted in terms of hydrogen ions liberated per iron atom (Fig. 2*a*) indicate that two, or nearly two, hydrogen ions are liberated per iron atom at a mol. ratio of phosphoric acid to ferric chloride of 1 : 1. The liberation of hydrogen ions in the titration of ferric chloride with sodium dihydrogen phosphate (0·7 mol. per iron atom at a mol. ratio of 1 : 1) is in accord with the equation

$$FeCl_3 + NaH_2PO_4 \rightleftharpoons [FeHPO_4]^+ + H^+ + Na^+ + 3Cl^-$$

It thus appears that the complex $[FeHPO_4]^+$ is present and is adsorbed by the resin together with simple ferric ions. At higher $H_3PO_4 : FeCl_3$ ratios the cationic complex is apparently replaced by an un-ionised or anionic complex, possibly $[Fe(HPO_4)_2]^-$, which is not adsorbed by the anion-exchanger in the presence of chloride. In fact, no complex ions are adsorbed by this exchanger from these solutions unless a high concentration of phosphate (Table 1*a*) or of chloride (Table 1*b*) is present.

Although the low adsorption of iron by the cation-exchanger is in accord with complex formation, evidence for cationic complexes comes only from the solutions containing the highest mol. ratio of hydrochloric acid to ferric phosphate (Table 2). The corresponding experiments with the anion-exchanger (Fig. 3*a*) show, however, that anionic complexes are formed in all the solutions. In Table 3 the data are interpreted in terms of the capacity of the resin on the supposition that various complexes are adsorbed.

TABLE 3. *Adsorption of a complex ion, free phosphate, and chloride by* I.R.A. 400–$PO_4$ (1·000 *g.*; *capacity* 2·1—2·4 *milliequiv./g.*) *from ferric phosphate–hydrochloric acid solutions.*

| | | | | | | |
|---|---|---|---|---|---|---|
| [Cl]/[Fe] in solution | 0·00 | 0·41 | 0·96 | 1·71 | 2·79 | 4·53 |
| [Cl]/[$PO_4$] in solution | 0·00 | 0·03 | 0·06 | 0·11 | 0·19 | 0·30 |
| Free phosphate adsorbed as $HPO_4''$, % * | 35 | 40 | 45 | 50 | 60 | 70 |
| Complex postulated | Total milliequivs. adsorbed/g. of resin | | | | | |
| $[Fe(PO_4)_3]^{6-}$ | 2·62 | 2·50 | 2·33 | 2·20 | 2·17 | 2·06 |
| $[Fe(HPO_4)_3]^{3-}$ | 1·74 | 1·95 | 1·81 | 1·80 | 1·85 | 1·98 |
| $[Fe(PO_4)_2Cl_2]^{5-}$ | — | 2·20 | 2·06 | 2·01 | 2·03 | 2·03 |
| $[Fe(PO_4)Cl_n]^{n-}$ | — | 1·91 | 1·79 | 1·81 | 1·87 | 2·00 |

* Remainder as $H_2PO_4'$; based on adsorption of phosphate and chloride by samples of known capacity from phosphoric–hydrochloric acid solutions having the same ratios of [Cl]/[$PO_4$].

It is apparent that, while adsorption of $[Fe(PO_4)_3]^{6-}$ or $[Fe(PO_4)_2Cl_2]^{5-}$ would account for the known capacity of the resin, the adsorption of ions such as $[Fe(PO_4)Cl_n]^{n-}$ (*e.g.*, $[Fe(PO_4)Cl_3]^{3-}$) would not. It is difficult, however, to reconcile the adsorption of $[Fe(PO_4)_2Cl_2]^{5-}$ ions, which should be present in increasing amount as the chloride ion concentration is raised, with the rapid decrease in adsorption of the complex (Fig. 3*a*). Thus it appears that the complex ion adsorbed in major amount is a triphosphatoferric ion. The high values calculated for the capacity of the resin on the basis of the adsorption of $[Fe(PO_4)_3]^{6-}$ when little or no chloride is present indicate that some $[Fe(HPO_4)_3]^{3-}$ ions are also adsorbed.

The decrease in adsorption of the complex ion with increasing mol. ratio of hydrochloric acid to ferric phosphate is attributed to the displacement to the right of equilibria such as :

$$[Fe(PO_4)_3]^{6-} \rightleftharpoons [Fe(HPO_4)_3]^{3-} \rightleftharpoons [Fe(HPO_4)_2]^- \rightleftharpoons [Fe(HPO_4)]^+ \rightleftharpoons [Fe]^{+++}$$

by reactions of the type :

$$[Fe(HPO_4)_3]^{3-} + 2H^+ \rightleftharpoons [Fe(HPO_4)_2]^- + H_3PO_4$$

(The co-ordination number of iron is presumably made up to four or six by co-ordination with water molecules.)

Since equilibria of the type postulated above would be displaced to the left by addition of phosphoric acid, the results obtained with the ferric chloride–phosphoric acid solutions can be explained on the same basis. Hydrochloric acid thus appears to function as a source of hydrogen ions and the close similarity of the results obtained when nitric acid was used in place of hydrochloric acid (Figs. 2*c*, 2*d*, and 3*b*; Table 4) supports this view.

Only with higher chloride-ion concentrations (Table 1*b*) does the formation of chloroferriphosphate complexes appear to be important.

TABLE 4. *Adsorption of iron and phosphate by Zeo-Karb* 225-H (0·500 *g.*) *from* 50 *ml. of a mixture of* 0·1M-*ferric nitrate* (pH 1·4) *with* 0·3M-*phosphoric acid.*

| Solution | | Resin, millimoles adsorbed/g. | | Solution | | Resin, millimoles adsorbed/g. | |
|---|---|---|---|---|---|---|---|
| $[PO_4]/[Fe]$ | pH * | Fe | $PO_4$ | $[PO_4]/[Fe]$ | pH * | Fe | $PO_4$ |
| 0·68 | 0·80 | 2·25 | 0·91 | 1·09 | 0·80 | 2·35 | 1·25 |
| 0·88 | 0·80 | 2·25 | 1·10 | 1·33 | 0·80 | 2·37 | 1·30 |

* Of solution in equilibrium with the resin.

The slight retention of phosphate from solutions containing iron, phosphate, and chloride by columns of Zeo-Karb 225 reported in Part I was presumably due to adsorption of $[FeHPO_4]^+$ ions. The fact that the retention was not greater can probably be ascribed to the difference in conditions. In the batch experiments, the solution was present in excess, the resin was apparently saturated, and time had been allowed for equilibrium to be established. In the column experiments, however, the resin was greatly in excess and was not saturated, while equilibrium conditions were not achieved.

## EXPERIMENTAL

The experimental procedure was the same as in Part I except for the following points.

*Preparation of Solutions.*—Electrolytic iron was used. For the chloride and phosphate solutions, a known volume of the acid of known strength was used and the solutions so obtained were oxidised with hydrogen peroxide as before.

*Apparatus.*—Because smaller quantities of resin were employed, it was possible to use smaller columns (1 cm. internal diam., 10 cm. long, above sintered disc).

*Procedure.*—At least 3 weeks, with frequent shaking, were allowed for solutions and resin to come to equilibrium. The solution was then filtered through the dry column and the filtrate kept for analysis and pH measurement. The resin was then transferred to the column and washed rapidly with water (*ca.* 50 ml.) under suction. The column was filled with water and the resin washed with a further 800 ml. of water before elution with 500 ml. of 2—3N-nitric acid. Aliquots of the eluate were used for analyses. The difficulty in eluting iron from a cation-exchanger reported by Goudie and Rieman (*Analyt. Chem.*, 1952, **24**, 1067) was not encountered.

In all cases, the sum of the iron adsorbed by the resin and that remaining in solution tallied closely with that originally present. Thus the possibility of complexes being decomposed on washing of the resins may be ruled out (cf. Leden, *Svensk Kem. Tidskr.*, 1952, **64**, 145). In the experiments represented in Fig. 1*c*, the phosphate content of the solutions in equilibrium with the resin was also checked and the total of phosphate originally present was accounted for.

*Analysis.*—Iron was determined, after elimination of nitric acid, by titration with standard potassium dichromate solution or, when only small amounts were present, colorimetrically with thiocyanate after precipitation of phosphate present with zirconium oxychloride. Phosphate was determined gravimetrically as ammonium phosphomolybdate. Chloride was determined as silver chloride. Blank experiments showed the nitric acid used for elution to be free from iron, phosphate, and chloride.

*Capacity of the Resins.*—The capacity of the cation exchanger was determined by passing 250 ml. of 0·5N-sodium chloride through a column containing 0·500 g. of resin in the hydrogen form and determining the acid liberated in the effluent. For the anion-exchanger 500 ml. of 2—3N-nitric acid were passed through a column containing 1·000 g. of the chloride form of the resin, and the chloride content of the effluent was determined.

The author thanks Dr. V. S. Griffiths for valuable discussions and Mr. R. F. Jameson for carrying out the colorimetric analyses.

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## 540. *Nitration in Sulphuric Acid. Part IX.* The Rates of Nitration of Nitrobenzene and Pentadeuteronitrobenzene.*

By T. G. Bonner, Freda Bowyer, and Gwyn Williams.

Within the limits of experimental error, the rates of nitration of nitrobenzene in 97·4% and in 86·7% sulphuric acid are identical with the rates of nitration of pentadeuteronitrobenzene in the same media. These results confirm Melander's demonstration (*Arkiv Kemi*, 1950, **2**, 211) that breakage of the C–H bond is not part of the rate-determining step in aromatic nitration, and extend it to more highly acid nitrating conditions.

Melander has shown (*Nature*, 1949, **163**, 599; *Arkiv Kemi*, 1950, **2**, 211) that the radioactive intensities in the products of nitration of benzene, toluene, bromobenzene, and naphthalene, each containing one appropriately situated nuclear tritium atom, are consistent only with the supposition that nitration at C–T and C–H bonds takes place at approximately the same speed. Melander derived minimum values for the velocity coeffient ratios $k_T/k_H$ for all stages of the nitrations and found them to lie between 0·74 and 0·85. It follows that the breakage of the C–H bond does not form part of the rate-determining step in aromatic nitration under the conditions of these experiments.

This conclusive result applies, in the first instance, to experimental conditions nearer to those of preparative nitration, with relatively high proportions of nitric acid and aromatic compound to sulphuric acid, and with moderately aqueous nitrating mixtures, than to the conditions of the kinetic nitration experiments in homogeneous systems initiated by Martinsen (*Z. physikal. Chem.*, 1904, **50**, 385; 1907, **59**, 605). In Melander's experiments, naphthalene was nitrated with a nitric acid–water mixture; but mixtures of nitric acid (*d* 1·40—1·42) and sulphuric acid (96—96·6%) were used for the other three compounds, and reaction was continued to the dinitration stage. Calculation from the quantities used gives typical reaction mixtures as approximately: benzene 0·0055, $HNO_3$ 0·043, $H_2SO_4$ 0·099, $H_2O$ 0·085 mole, molar ratio $H_2O/H_2SO_4 = 0·86$; and toluene 0·0046, $HNO_3$ 0·053, $H_2SO_4$ 0·124, $H_2O$ 0·104 mole, molar ratio $H_2O/H_2SO_4 = 0·84$. In these nitrations, only the conversion of nitrobenzene into *m*-dinitrobenzene requires a sulphuric acid–water mixture acid enough to convert a considerable proportion of nitric acid into nitronium ion (Hetherington and Masson, *J.*, 1933, **105**; Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955; Williams and Lowen, *J.*, 1950, 3312). The molar ratio $H_2O/H_2SO_4$ in the acid employed corresponds to a nitration medium considerably more aqueous than the medium ($H_2O/H_2SO_4 \sim 0·58$) giving maximum rate in the homogeneous nitration of nitrobenzene (Bonner *et al.*, *loc. cit.*). Oleum was used in the nitrating acid for bromobenzene but here also the molar ratio $H_2O/H_2SO_4$ was not less than 0·79.

Nitrating acids with these relatively high water (and nitric acid) contents must contain considerable concentrations of the basic species bisulphate ion; and the conditions of nitration are different from those prevailing in kinetic nitration experiments in homogeneous solution in concentrated sulphuric acid (Part IV, *J.*, 1947, 474; Part VIII, *loc. cit.*). For example, the reaction mixture in 97·4% sulphuric acid (see Table) has the composition: nitrobenzene 0·0075, $HNO_3$ 0·0017, $H_2SO_4$ 0·909, $H_2O$ 0·132 mole, molar ratio $H_2O/H_2SO_4 = 0·145$. It is in the most acid conditions, if anywhere, that the separation of the proton might have kinetic significance in nitration.

In order to put it beyond doubt that Melander's demonstration, that there is no hydrogen isotope effect in nitration, applies also to highly acid conditions, we have compared directly the rates of nitration of nitrobenzene and pentadeuteronitrobenzene, with small reagent concentrations, in homogeneous solution. In the media employed the rates of nitration are given by the equation $-d[HNO_3]/dt = k_2[ArNO_2][HNO_3]$, since $\log\{[ArNO_2]/[HNO_3]\}$ is linear with time (see Figure). The final results for velocity coefficients are given in the Table. The observed identity of nitration rate for nitro-

* Part VIII, *J.*, 1952, 3274.

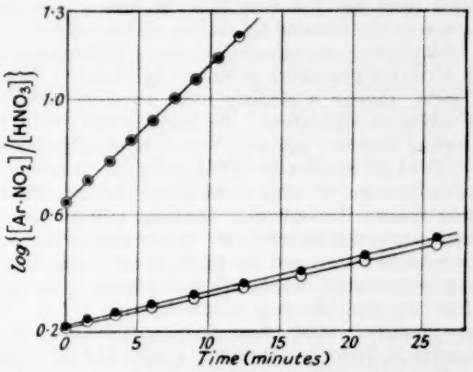
benzene and pentadeuteronitrobenzene, in both media, is not likely to have been simulated through isotope exchange between aromatic compound and nitrating acid; because (*a*) it could only be due *either* to genuine identity of nitration rate at C–H and C–D bonds *or* to complete transfer of deuterium from aromatic ring to nitrating acid before measurements

*Rates of nitration at* 25° ($k_2$ in l. mole$^{-1}$ min.$^{-1}$; concentrations in terms of M).

| Medium | Expt. | Nitrobenzene | | | Expt. | Deuteronitrobenzene | | |
|---|---|---|---|---|---|---|---|---|
| $H_2SO_4$, % | No. | $[C_6H_5{\cdot}NO_2]$ | $[HNO_3]$ | $k_2$ | No. | $[C_6D_5{\cdot}NO_2]$ | $[HNO_3]$ | $k_2$ |
| 97·4 | 130 | 0·1498 | 0·03402 | 0·941 | 129 | 0·1498 | 0·03442 | 0·938 |
| | 132 | 0·1498 | 0·03419 | 0·954 | 131 | 0·1498 | 0·03397 | 0·942 |
| 86·7 | 133 | 0·05015 | 0·03040 | 1·34 | 135 | 0·04963 | 0·03056 | 1·29 |
| | 134 | 0·05023 | 0·03205 | 1·33 | 136 | 0·05017 | 0·02998 | 1·27 |

were started; (*b*) rapid deuterium exchange between a nitro-aromatic compound and sulphuric acid is improbable (cf. Ingold, Raisin, and Wilson, *J.*, **1936**, 915, **1637**); and (*c*) we have found that pentadeuteronitrobenzene does not change its density after exposure to 97·3% sulphuric acid, at 20°, for a longer time than that required for the nitration experiments (see Experimental section).

*Nitration of*: ● *nitrobenzene.*
○ *pentadeuteronitrobenzene.*




Earlier results, with a less exactly characterised specimen of pentadeuteronitrobenzene, pointed to the same general conclusion as the results in the Table. With $k_H$ and $k_D$ referring, respectively, to replacement of protium and deuterium atoms, the results were: in 97·9% sulphuric acid (0·025M-$Ar{\cdot}NO_2$), $k_H = 0{\cdot}74$; $k_D = 0{\cdot}67, 0{\cdot}69$. In 97·6% sulphuric acid (0·15M-$Ar{\cdot}NO_2$), $k_H = 0{\cdot}87, 0{\cdot}89$; $k_D = 0{\cdot}82, 0{\cdot}84$.

We are indebted to Dr. J. C. D. Brand, of the University of Glasgow, for the results of measurements of nitration velocity (made by following the change in extinction coefficient, Brand and Paton, *J.*, 1952, 281) for the same sample of pentadeuteronitrobenzene in 10% oleum (102·25% $H_2SO_4$). With excess of nitric acid (0·108 molal) and $9 \times 10^{-5}$ molal concentration of aromatic compound, the first-order nitration velocity coefficients were: for $C_6H_5{\cdot}NO_2$, $k_1 = 0{\cdot}0344, 0{\cdot}0341$; for $C_6D_5{\cdot}NO_2$, $k_1 = 0{\cdot}0320, 0{\cdot}0323$. In this medium, the greater part (75—80%) of the aromatic compound exists as its (cation) conjugate acid. It is not certain that the extent of cation formation is the same for the protium and deuterium compounds.

If the whole of the difference between the zero-point energies of a C–H and of a C–D bond (*ca.* 2 kcal./mole) were to influence nitration rates, then the ratio $k_D/k_H$ could be as low as 0·035. It is clear, even in the most acid media, that the fission of the C–H bond does not help to determine rate of nitration (cf. Melander, *loc. cit.*). The hypothesis of bisulphate-ion catalysis (Part IV, *loc. cit.*) cannot be sustained.

## Experimental

*Preparation of Pentadeuteronitrobenzene.*—Hexadeuterobenzene was prepared by the method of Ingold, Raisin, and Wilson (*loc. cit.*; Best and Wilson, *J.*, 1946, 239). 10 ml. of benzene

(B.D.H. " for molecular weight determinations "; distilled from phosphoric oxide; $d_{25}^{25}$ 0·8760) were shaken for 5 days with 60 g. of deuterosulphuric acid, containing 51 moles % of $D_2SO_4$ and 49 moles % of $D_2O$, made by distilling sulphur trioxide (80 g.) into 35 ml. of Norsk Hydro Heavy Water, containing 99·75 atoms % of D, standardising the product by titration with 0·1N-sodium hydroxide, and final adjustment to 83·8% (w/w) $D_2SO_4$ by distilling in a further 11·4 g. of sulphur trioxide. After this first shaking, the benzene was distilled away and shaken a second time for 5 days with a fresh portion (60 g.) of the same acid. It was then distilled (*a*) on to dry barium oxide, (*b*) after several hours, on to phosphoric oxide, and (*c*) after 3 hr., into a clean receiver. At this stage the benzene had $d_{25}^{25}$ 0·09421, corresponding to a content 92·0 atoms % of D. It was then shaken a third time for 5 days, but this time with 60 g. of 83·8% deuterosulphuric acid prepared from heavy water containing 99·95 atoms % of D. It was then treated with barium oxide and phosphoric oxide as before. It now had $d_{25}^{25}$ 0·9456 corresponding to content 99·3 atoms % of D (Weldon and Wilson, *J.*, 1946, 235); the yield was 5·7 g.

All the benzene distillations referred to were conducted in all-glass apparatus, with oil-pump vacuum, and with appropriate heating baths and refrigerants. In the preparation of deuterosulphuric acid (cf. Best and Wilson, *loc. cit.*), it was found satisfactory to distil sulphur trioxide slowly (without vacuum) from a vessel attached by a ground joint, through a capillary, into two flasks in series, cooled by ice–water, one empty and one containing deuterium oxide, protected from the atmosphere, through a capillary, by a sulphuric acid trap. Sulphur trioxide was driven from the first flask into the heavy water after sealing off the first capillary; and the apparatus was isolated by sealing off the second.

*Nitration of Hexadeuterobenzene.*—Preliminary experiments with ordinary benzene showed the nitration procedure described by Masson (*Nature*, 1931, **128**, 726) to be the most profitable in yield, though a slightly more aqueous nitrating acid was found to be advantageous in excluding all dinitration. To minimise the (small) risk of isotope exchange during nitration, the nitrating acid was made up with deuterosulphuric acid. The composition was $D_2SO_4$ (18·4 g.), $H_2O$ (3·14 g.), anhydrous $HNO_3$ (5·29 g.). Into this were run in, during 70 min., 5·7 g. of hexadeuterobenzene through a capillary, the temperature being kept at 45°, and the reaction flask being shaken throughout. Shaking, still at 45°, was continued for a further 230 min. The temperature was raised to 60° at the end of the reaction, after which the reaction mixture was poured into water, and the product was separated, washed with sodium carbonate solution and then with water, dried with phosphoric oxide and distilled. The yield was 7·7 g. (88·9%). After two distillations a middle fraction (5·5 g.; b. p. 64—65°/5 mm., 215—217°/711 mm.) of very faintly yellow *pentadeuteronitrobenzene* was collected (Found: N, 11·1. $C_6D_5O_2N$ requires N, 10·9%). It had $d_{25}^{25}$ 1·2533 and $n_D^{20}$ 1·5504.

*Deuterium Content.*—We are very much indebted to Dr. R. I. Reed of the University of Glasgow for a mass-spectrographic examination of the water formed by combustion of our product. The result showed its deuterium content to be >99·5 atoms %.

*Nitrobenzene.*—" AnalaR " material was dried and distilled and purified by fractional crystallisation to constant m. p. 5·82°.

*Velocity Measurements.*—The rate of nitration was followed by measuring the residual nitric acid concentration at known time intervals. The methods of experiment and of analysis of reaction mixtures and media were as described in Part VIII (Bonner, Bowyer, and Williams, *loc. cit.*).

*Test for Deuterium Exchange during Nitration.*—A specimen of pentadeuteronitrobenzene (2·3 g.) was dissolved in 97·3% sulphuric acid (5 ml.) and kept at 20° for 1·75 hr. It was then recovered by dilution with 16 ml. of water, repeated extraction with ether, repeated washing with water, drying, and distillation under reduced pressure. The material had *d* 1·2520 and 1·2518, respectively, before and after exposure to sulphuric acid. Since ordinary nitrobenzene has $d^{25}$ 1·198, deuterium exchange with sulphuric acid during a nitration experiment (requiring <30 min.) is evidently inappreciable.

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## 541. *Oxygen Exchange between Nitric Acid and Water. Part III.* Catalysis by Nitrous Acid.*

By C. A. Bunton, E. A. Halevi, and D. R. Llewellyn.

The exchange of oxygen between nitric acid and water has been followed isotopically at 0°. In the concentration range 8—28 mole % nitric acid, exchange only occurs in the presence of " nitrous acid." The kinetic effects of variations in nitric and nitrous acid concentrations have been studied, and are interpreted in terms of a two-stage mechanism, involving exchange between water and nitrous acid, and between nitrous acid and nitric acid.

In an investigation of the exchange of oxygen between nitric acid and water, it was found that, while the direct rate of exchange in aqueous nitric acid containing less than 40 mole % of $HNO_3$ was too slow to be measurable at 0° (Part I, Bunton, Halevi, and Llewellyn, *J.*, 1952, 4913), the presence of minute amounts of the lower oxides of nitrogen (here given the general name of " nitrous acid ") induces exchange. In the concentration range of nitric acid 8—28 mole %, the exchange can be followed conveniently with nitrous acid concentration $2—12 \times 10^{-3}$ mole %.

The method of following the exchange was similar to that described in Part I, with the modification that " nitrous acid " was either allowed to develop or added as sodium nitrite. The source of the nitrous acid did not affect the experimental results, and the minute amounts of sodium cations had no apparent effect. The nitrous acid was determined during the run, and, as in some runs variations in its concentrations were observed, instantaneous rates of exchange were estimated. As it was found that for a given nitric acid concentration, the instantaneous rate of exchange depended only on the nitrous acid concentration, and not on its source or previous history, we may conclude that the catalysis by nitrous acid does not involve a slow chemical interconversion between the various forms of " nitrous acid," although it may involve isotopic exchange between these forms.

*Formal Treatment of Ternary Exchange.*—In the present work, as in Part I, the rates, $R$, of oxygen exchange between nitric acid and water were evaluated from the expression :

$$R = -\frac{3[HNO_3][H_2O]}{3[HNO_3] + [H_2O]} \cdot \frac{d}{dt}(\alpha_\infty - \alpha_t) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the concentrations are expressed in mole %, and $\alpha_\infty$ and $\alpha_t$ represent the isotopic abundance of $^{18}O$ in the nitric acid at complete exchange and at time $t$, respectively.

Equation (1) was derived for a two-component system, but in exchange catalysed by nitrous acid we must consider, at least formally, two steps in the overall exchange, one between nitrous and nitric acids, and the other involving nitrous acid and water. This does not exclude the possibility that the two steps may be concerted, or that each exchange may involve more than one chemical reaction.

As the system is assumed to be in stoicheiometric equilibrium, the exchange reaction may be expressed in terms of two independent exchanges, each involving the nitrous acid catalyst :

$$AX_n \overset{R_1}{\longleftrightarrow} CX_p \overset{R_2}{\longleftrightarrow} BX_m$$

We assume that one atom only is transferred per unit act of exchange ; then if $\alpha$, $\beta$, and $\gamma$ are the isotopic abundances of the three species, $AX_n$, $BX_m$, and $CX_p$ respectively,

$$n[AX_n] \cdot (d\alpha/dt) = R_1(\gamma - \alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

and

$$-m[BX_m] \cdot (d\beta/dt) = R_2(\beta - \gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

* Part II, *J.*, 1952, 4917.

If the concentration of $CX_p$ is low, the stationary-state treatment gives:

$$R_1(\gamma - \alpha) = R_2(\beta - \gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$n[AX_n] \,.\, (d\alpha/dt) = R_1R_2(\beta - \alpha)/(R_1 + R_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and therefore the net rate of exchange $R$ is given in terms of the two component steps by:

$$R = R_1R_2/(R_1 + R_2)$$

Preliminary results on the effect of [nitrous acid] on the overall rate of exchange indicated a variation of kinetic order with respect to [nitrous acid], from 1 to 2, and we assumed a dependency of the form:

$$R_1 = k_1 [\text{“ } HNO_2 \text{ ”}]; \; R_2 = k_2 [\text{“ } HNO_2 \text{ ”}]^2$$

*i. e.*,

$$R = k_1k_2 [\text{“ } HNO_2 \text{ ”}]^2/(k_1 + k_2 [\text{“ } HNO_2 \text{ ”}]) \quad . \quad . \quad . \quad . \quad (5)$$

Experimentally the order with respect to [nitrous acid] was estimated by plotting log $R$ against log [nitrous acid]; this pre-supposes that the rate is expressible in the form:

$$R = k [\text{“ } HNO_2 \text{ ”}]^n$$

where $n$ is the order. Obviously equation (5) cannot be expressed in this form and the “ kinetic order ” as derived by this method has no precise significance except when the order is integral. However this kinetic order is relatively insensitive to small variations in [nitrous acid], and does give an indication of transition from one kinetic form to another.

Our general procedure was to carry out a block of runs at a definite nitric acid concentration, varying the nitrous acid concentration between 2 and 12 $\times$ $10^{-3}$ mole %. This gave an indication of the apparent kinetic order with respect to [nitrous acid]. The values of the exchange rate interpolated at an arbitrary concentration of 5 $\times$ $10^{-3}$ mole % of nitrous acid are quoted for the various concentrations of nitric acid. The general procedures for determining the rate and kinetic form of the isotopic exchange are illustrated by Tables 1 and 2. The limiting factor in our kinetic measurements is probably the determination of [nitrous acid], which is carried out colorimetrically after dilution in

TABLE 1.

| [$HNO_3$] (mole %) | $10^3$ [$HNO_2$] (mole %) | $10^3R$ (mole % sec.$^{-1}$) | $10^3R$ * (interpolated) (mole % sec.$^{-1}$) | Order |
|---|---|---|---|---|
| 8·2 | 3·0 | 0·375 | 0·62 | 1·0 |
| | 8·0 | 0·991 | | |
| 10·5 | 2·3 | 0·658 | 1·72 | 1·2 |
| | 6·8 | 2·49 | | |
| 16·0 | 1·9 | 3·11 | 13·8 | 1·6 |
| | 6·8 | 23·4 | | |
| 16·7 | 4·9 | 16·0 | 17·8 | 1·7 |
| | 24·0 | 230 | | |
| 19·7 | 5·0 | 39·2 | 39·5 | 1·8 |
| | 9·4 | 131 | | |
| 21·8 | 2·4 | 20·1 | 97·8 | 2·0 |
| | 3·0 | 35·2 | | |
| | 4·5 | 82·0 | | |
| 23·6 | 2·7 | 39·8 | 122 | 2·0 |
| | 3·8 | 62·6 | | |
| | 5·5 | 141 | | |
| | 5·6 | 173 | | |
| 25·1 | 3·9 | 116 | 166 | 1·3 |
| | 6·7 | 231 | | |
| | 11·9 | 462 | | |
| 28·3 | 2·2 | 70·3 | 179 | 1·1 |
| | 4·8 | 171 | | |

* Denotes rate interpolated at [$HNO_2$] = 5 $\times$ $10^{-3}$ mole %.

water (Part I). The effect of this uncertainty, and of the variation in [nitrous acid] is most serious in runs in which the kinetic order tends to second.

No consideration is given to the mechanism of the nitrous acid decomposition process, and as the rate of exchange depends only on the instantaneous concentration of nitrous acid, and not on its rate of decomposition, the reactions involved in the exchange are not those of the decomposition of nitrous acid.

*Discussion.*—Any reaction scheme for exchange between water and nitric acid catalysed by nitrous acid must explain the change of kinetic order, with respect to [nitrous

acid], with increasing [nitric acid], from first to second, and back to first above 24 mole % $HNO_3$. It must also explain the effect of $[HNO_3]$ on the overall rate of exchange at fixed [nitrous acid], say $5 \times 10^{-3}$ moles %. The $[HNO_3]$-rate curve shows a sigmoid form, whose exact shape depends on the concentration of nitrous acid arbitrarily chosen (see Fig., lower full curve).

The change of kinetic form with increasing nitric acid concentration may be due to a number of causes: (*a*) Two independent simultaneous reactions, with different kinetic orders, which depend on acidity. (*b*) Two consecutive exchange reactions of different kinetic orders, each of which leads to exchange between nitrous acid and one of the other two components. (*c*) The rate-determining reaction may be of a fixed order with respect to one or other of the nitrous acid species, but its "apparent kinetic order" relative to analytical nitrous acid may vary as a result of the changing relation between the concentrations of the active species and of the total nitrous acid.

The experimental results require that there must at some stage of the exchange be a reaction of the second order with respect to [nitrous acid]. This stage could involve $N_2O_4$ only in the unlikely event that the bulk component of nitrous acid is $NO_2$. The only other species that can reasonably be assumed to participate in a reaction showing second-order kinetics is $N_2O_3$, and this only when it is not the bulk component of nitrous acid. Dinitrogen trioxide, exchanging its oxygen with water, by the reaction:

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2$$

or the kinetically equivalent reaction:

$$N_2O_3 + H_2O \rightleftharpoons H_2NO_2^+ + NO_2^-$$

would lead to exchange between nitrous acid and water of rate proportional to $[N_2O_3]$.

However, a number of other plausible reactions may be eliminated from consideration. The reaction:

$$HNO_2 + HNO_3 \rightleftharpoons N_2O_4 + H_2O$$

and its protonated equivalent, would lead to a one-step exchange between nitric acid and water, which would be of the first order with respect to [nitrous acid] in all conditions.

Similarly, the formation of the nitrosonium ion by direct ionisation of the nitrous acidium ion by the reaction:

$$H_2NO_2^+ \rightleftharpoons NO^+ + H_2O$$

would require a first-order exchange between nitrous acid and water, whose rate would increase indefinitely with increasing acidity. This could not explain the change of kinetic order, and the net rate could be slow only if the reaction $NO^+ + NO_3^- \rightleftharpoons N_2O_4$, giving exchange between nitrous and nitric acids, were unaffected by increasing nitric acid.

The observed kinetic form is explained by the following exchange sequence:

$$H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

giving exchange between water and nitrous acid, and exchange between nitrous and nitric acids by the reactions:

$$N_2O_3 \rightleftharpoons NO^+ + NO_2^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

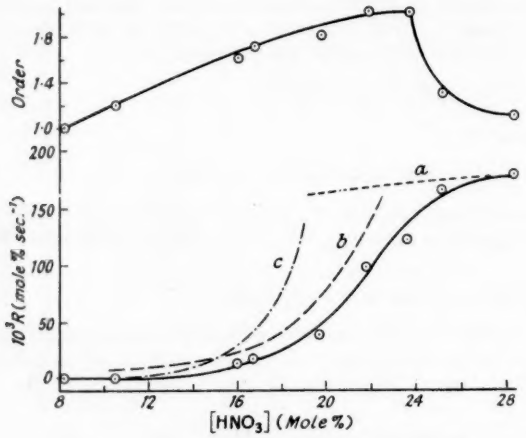
We assume that at low acidities the nitrous acid–water exchange is fast, and that the nitrous–nitric acid exchange by the reactions (*b*) and (*c*) is rate determining. If $[N_2O_3] \gg [N_2O_4]$ the total rate of reaction (*c*) may be less than that of (*b*), with reaction (*c*) the rate-determining step of the exchange. With $HNO_2$ the bulk component of nitrous acid, reactions (*a*) and (*b*), depending on $[N_2O_3]$, would both be of second order with respect to [nitrous acid], and reaction (*c*) is the only reaction which would show this first-order dependence of exchange rate on nitrous acid.

The rates of reactions (*b*) and (*c*) should both increase rapidly with an increase of nitric

acidity, but protonation of $NO_2^-$ [by decreasing the rate of the back reaction and therefore of the forward reaction of (*b*)], will make the acid catalysis of (*b*) less effective than that of (*c*). The rate of exchange is given by the total number of molecules undergoing reaction, and an increase of the specific rate of (*c*) may make reaction (*b*), involving the ionisation of $N_2O_3$, the rate-determining step of the exchange, before the concentration of $N_2O_4$ approaches that of $N_2O_3$. The net exchange will then be of first order with respect to $[N_2O_3]$, and of second order with respect to [nitrous acid], provided that $N_2O_3$ is not the bulk component of the nitrous acid.

The exchange between nitrous and nitric acids by reactions (*b*) and (*c*), should be continuously acid-catalysed, and the levelling of rate which we observe must be due to reaction (*a*) becoming rate-determining.

We have assumed that at low acidities the bulk component of nitrous acid is molecular $HNO_2$, or its protonated or depronated ions, but that in more acid solutions it will be progressively dehydrated to $N_2O_3$. The rate of reaction (*a*) will then no longer increase rapidly, and as $N_2O_3$ becomes the bulk nitrous acid component, the order will tend towards first.




*Dependence of rate and order on nitric acid concentration.*

The experimentally observed variations in rate and kinetic order, with increasing nitric acidity, can therefore be qualitatively reproduced quite simply, as the resultant of the three reactions considered. This is illustrated schematically in the Figure. This reaction scheme requires that at low nitric acidity the bulk nitrous acid component is molecular $HNO_2$, but that with increasing nitric acid progressive dehydration makes $N_2O_3$ the bulk component above *ca.* 25 moles %. At higher concentrations it is known that the bulk component of nitrous acid is $N_2O_4$, and that in pure nitric acid it is ionised to give nitrosonium ions (which probably exist as $\overset{+}{N}O{\cdot}NO_2$). Therefore at higher nitric acid concentrations exchange should occur by such reactions as :

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$
$$NO^+ + H_2O \rightleftharpoons H_2NO_2^+$$

Unfortunately decomposition of nitrous acid occurs so rapidly in nitric acid above *ca.* 32 moles % that quantitative measurements of exchange rate could not be made in this region, although qualitatively it appeared that the exchange was not instantaneous. Above this region exchange between nitric acid and water occurs in the absence of nitrous acid (Part I).

The suggested reaction scheme implies that in nitrosations in aqueous acidic media, involving the nitrosonium ion, $NO^+$, this ion is derived from the neutral molecules $N_2O_3$, or $N_2O_4$, rather than by dehydration of the nitrous acidium ion, $H_2NO_2^+$. In this respect

the situation is not analogous to nitration, where the nitronium ion, $NO_2^+$, is derived from $H_2NO_3^+$. In nitration where the bulk reactivity of the aromatic compound is high compared to that of water, zero-order kinetics are observed (Hughes, Ingold, and Reed, *J.*, 1950, 2400), but in nitrosations where $NO^+$ is derived from $N_2O_3$ observation of zero-order kinetics will require the organic compound to be more reactive than the highly nucleophilic nitrite ion, and such a compound would probably react directly with $N_2O_3$, itself a strong nitrosating agent (Hughes, Ingold, and Ridd, *Nature*, 1950, **166**, 642).

It is not easy to correlate the evidence of isotopic exchange with that from other sources, particularly under the experimental conditions used. However, independent evidence for the postulated reactions (*a*) is provided by the kinetic study of diazotisation in aqueous acidic media (Hughes, Ingold, and Ridd, *loc. cit.*); and ionisations of $N_2O_3$ and $N_2O_4$, reactions (*b*) and (*c*), have been discussed by Hughes, Ingold, and Reed (*loc. cit.*) in their consideration of the nitrous acid anticatalysis of aromatic nitration. Also spectroscopic and conductometric measurements in 100% nitric acid show that $N_2O_4$ is completely ionised under these conditions (Goulden and Millen, *J.*, 1950, 2620).

## Experimental

*Materials.*—Nitric acid and isotopically enriched water were prepared and purified by the methods outlined in Part I (*loc. cit.*).

*Kinetic Procedure.*—Solutions were made up by weight, and the general methods were those outlined in Part I (*loc. cit.*), except that no sulphamic acid was added, and nitrous acid was allowed to develop, or its concentration augmented by the addition of sodium nitrite. The rates of exchange (irrespective of labelling) were calculated from the isotopic data as previously described. Two typical runs are illustrated in Table 2.

Table 2. *Nitrous-acid-catalysed exchange, at 0°.*

Run No. 13. $[HNO_3]$ = 8·2 mole %. Abundance of heavy water ($\beta_0'$) = 1·76 atoms % excess. Final abundance of nitric acid ($\alpha_\infty'$) = 1·392 atoms % excess.

| $t$ (hr.) | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| $\alpha'$ | 0·091 | 0·176 | 0·264 | 0·337 | 0·404 | 0·460 | 0·522 |
| $\log_{10}(\alpha_\infty' - \alpha')$ | 0·114 | 0·085 | 0·052 | 0·023 | $\bar{1}$·995 | $\bar{1}$·969 | $\bar{1}$·939 |
| $10^3$ $[HNO_2]$ (moles %) | 2·99 | 3·14 | 2·84 | 2·99 | 2·74 | 2·70 | 2·44 |

$R = 3{\cdot}75 \times 10^{-4}$ mole % sec.$^{-1}$.

Run No. 63. $[HNO_3]$ = 28·31 mole %. Abundance of heavy water ($\beta_0'$) = 1·72 atoms % excess. Final abundance of nitric acid ($\alpha_\infty'$) = 0·787 atom % excess.

| $t$ (min.) | 0 | 3 | 6 | 9 |
|---|---|---|---|---|
| $\alpha'$ | 0·240 | 0·414 | 0·500 | 0·582 |
| $\log_{10}(\alpha_\infty' - \alpha')$ | $\bar{1}$·738 | $\bar{1}$·572 | $\bar{1}$·458 | $\bar{1}$·312 |
| $10^3$ $[HNO_2]$ (moles %) | 2·16 | — | 2·25 | 2·14 |

$R = 7{\cdot}03 \times 10^{-3}$ mole % sec.$^{-1}$.

*Determination of Nitrous Acid.*—The lower oxides of nitrogen were determined, during each kinetic run, after dilution in water, as described in Part I. This modification of the Griess–Ilosvay method depends on diazotisation in acid solution and coupling in alkaline solution, and the colour development is independent of time. It is probable that the measurement of nitrous acid at such low concentrations (*ca.* $10^{-3}$ moles %) is the limiting factor in the accuracy of our kinetic method.

The authors are indebted to Professors E. D. Hughes, F.R.S., and C. K. Ingold, F.R.S., for their continued interest. They are grateful to the Humanitarian Trust and the Friends of the Hebrew University for a maintenance grant to one of them (E. A. H.).

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University College, London. [*Received, April 27th*, 1953.]

## 542. *The Polymerizability of Methyl α-tert.-Butylacrylate. Part II.**

By J. W. C. Crawford.

The oxidation product dimethylmalonic acid, and the ultra-violet absorption spectrum of the ester prepared by dehydration of methyl tetramethyl-lactate, indicate that it is methyl 2 : 2 : 3-trimethylbut-3-enoate, formed by a *neo*pentyl rearrangement during the dehydration, and not methyl α-*tert.*-butylacrylate. α-*tert.*-Butylacrylic acid has been prepared by the Mannich synthesis from *tert.*-butylmalonic acid, and its structure confirmed. The methyl ester does not yield macromolecular polymers, but gives a considerable yield of dimer under the influence of sodium in liquid ammonia.

Crawford and Swift (Part I *) described unsuccessful attempts to induce ethenoid polymerization of methyl α-*tert.*-butylacrylate, obtained by dehydrating methyl tetramethyl-lactate with phosphoric oxide in presence of molar amounts of dimethylaniline. It was subsequently found that oxidation of the hydrolyzed ester with permanganate gave dimethylmalonic acid instead of the expected trimethylacetic acid. This led to the conclusion that during dehydration of the tetramethyl-lactate a *neo*pentyl rearrangement of the carbonium ion (I) occurred, with ultimate production of methyl 2 : 2 : 3-trimethylbut-3-enoate (II) instead of the expected methyl α-*tert.*-butylacrylate. This was supported by the resemblance of the ultra-violet absorption spectrum of the ester (*A*), to that of ethyl but-3-enoate (*B*), and its difference from that of methyl methacrylate (*C*) which has the form characteristic of αβ-unsaturated acid derivatives (Goodeve, *Trans. Faraday Soc.*, 1938, **34**, 1239) (see Fig.).

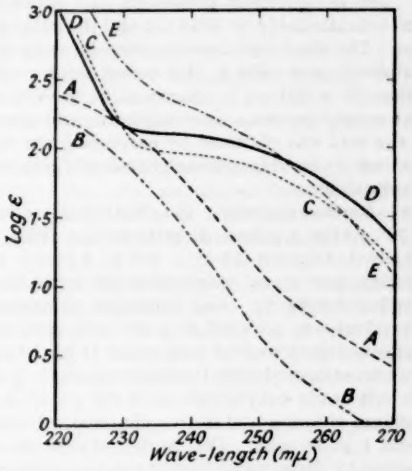
$Me_3C\cdot\overset{+}{C}Me\cdot CO_2Me$ (I) $\qquad CH_2{:}CMe\cdot CMe_2\cdot CO_2Me$ (II) $\qquad [Me_3C\cdot CH(CO_2Me)\cdot CH_2]_2$ (III)

α-*tert.*-Butylacrylic acid has been prepared by condensation of *tert.*-butylmalonic acid with formaldehyde and dimethylamine (cf. Mannich and Ganz, *Ber.*, 1922, **55**, 3486). The malonic acid has become readily available through Wideqvist's synthesis of the ester by condensation of *iso*propylidenemalonic ester with methylmagnesium iodide (*Arkiv Kemi, Min., Geol.*, 1946, **23**, *B*, No. 4). The Mannich reaction was incomplete, and led to small yields of α-*tert.*-butylacrylic acid, but much of the unchanged butylmalonic acid could be recovered and used again, with an acceptable overall yield of butylacrylic acid. The probable course of the Mannich reaction made it appear unlikely that rearrangement would occur during the synthesis; in any case, the structure of the butylacrylic acid was confirmed by formation of trimethylacetic acid in quantity on oxidation with permanganate. Methyl α-*tert.*-butylacrylate was prepared by direct esterification of the acid with methanol. Examination was made of the proposition that the butylacrylic structure could pass into the 2 : 2 : 3-trimethylbut-3-enoic structure during the esterification, through union with a proton to form the carbonium ion (I), followed by rearrangement, and proton elimination. However, when methyl butylacrylate was heated with the same methanol–sulphuric acid mixture as was used in the esterification, for 24 hours, there was no increase in refractive index or density: it was concluded that no significant rearrangement had occurred. Support for an αβ-unsaturated structure for the new ester and acid came from the resemblance of their ultra-violet spectra (*D*, *E* respectively) to that of methyl methacrylate (*C*). The ester, re-treated as above, gave the same spectrum as (*D*).

The methods described in Part I were used for investigation of the polymerizability of methyl α-*tert.*-butylacrylate. Prolonged heating with benzoyl peroxide, or long exposure in borosilicate glass to ultra-violet radiation, failed to produce a macromolecular polymer. A considerable yield of nitrogen-free, saturated liquid dimer, $C_{16}H_{30}O_4$, was obtained by

* Part I, *J.*, 1952, 1220.

the action of a solution of sodium in liquid ammonia; this was in contrast to the behaviour of methyl 2 : 2 : 3-trimethylbut-3-enoate, which yielded under the same conditions a negligible amount (0·5%) of material approximating in molecular weight to dimer. The difference seems to result from the comparatively ready activation of the butylacrylate, because of the influence of the carbomethoxy-group adjacent to the ethylene bond. Failure of the butylacrylate to propagate macromolecular polymer appears, as was discussed in Part I, to be the result of the steric effect of the α-*tert.*-butyl groups. A head-to-head




*Absorption spectra in* n-*hexane.*
*A, Methyl* 2,; 2 : 3-*trimethylbut-3-enoate.*
*B, Ethyl vinylacetate.*
*C, Methyl methacrylate.*
*D, Methyl* α-tert.-*butylacrylate.*
*E,* α-tert.-*Butylacrylic acid.*

saturated dimer (III) (methyl αδ-di-*tert.*-butyladipate) could, however, be formed without serious interference of this kind. Formation of (III) under the influence of the sodium appears analogous to the formation of 1 : 1 : 4 : 4-tetraphenylbutane from the sterically hindered 1 : 1-diphenylethylene by treatment of the latter with sodium in liquid ammonia (Wooster and Ryan, *J. Amer. Chem. Soc.*, 1934, **56**, 1133).

## Experimental

*Hydrolysis and Oxidation of the Unsaturated Ester from Methyl Tetramethyl-lactate.*—The ester (1·42 g., 0·01 mole) was hydrolyzed under reflux on the water-bath for 16 hr. with alcoholic 0·5N-potassium hydroxide (50 c.c.). The product was diluted with water, and alcohol boiled off. The residue, diluted to 300 c.c., was stirred at 20° with potassium permanganate (5·3 g. equiv. to 5 O). Decolorization was complete after 25 hr. A further 0·2 g. of permanganate was unreduced 25 hr. later. Excess of permanganate was reduced with sodium sulphite solution, the filtrate from manganese dioxide evaporated nearly to dryness on the water-bath, acidified with hydrochloric acid (*d* 1·18; 3·5 c.c.), and extracted five times with ether, and the combined extracts were neutralized with N-sodium hydroxide (phenolphthalein). The solution of sodium salt was concentrated, slightly acidified with hydrochloric acid, and heated under reflux for 2 hr. with *p*-bromophenacyl bromide (1·6 g.) and 95% alcohol (7 c.c.). The crystalline ester obtained was recrystallized from alcohol and had m. p. 128—128·5° (Found: Br, 30·4. Calc. for $C_{21}H_{18}O_6Br_2$: Br, 30·4%). Authentic *p*-bromophenacyl dimethylmalonate had m. p. 128·5—129°.

*Synthesis of Methyl* α-tert.-*Butylacrylate.*—*Ethyl* tert.-*butylmalonate.* Repetition on a five-fold scale of Wideqvist's synthesis (*loc. cit.*) gave the same yield (39%) of ester as recorded by the author. The side-reactions mentioned by Wideqvist were reduced by lowering the temperature of reaction of ethyl *iso*propylidenemalonate and methylmagnesium iodide to −20°, and by increasing the amount of solvent ether used, to prevent deposition at this temperature of viscous intermediate which interfered with stirring. To a Grignard solution (from methyl iodide, 600 g., magnesium, 102 g., and ether, 1050 c.c.), cooled to −15° to −20°,

with stirring, ethyl *iso*propylidenemalonate (750 g.) in ether (750 c.c.) was added during 65 min. The mixture was allowed to warm to −5° during 40 min., and decomposed on cracked ice (2 kg.). Magnesia was dissolved by addition of hydrochloric acid, the ethereal layer washed twice with water, once with dilute sodium sulphite solution, and twice again with water, and dried ($CaCl_2$), and solvent was removed. Fractionation of the crude ester through a 9″ Vigreux column gave ethyl *tert.*-butylmalonate, b. p. 102—105°/11 mm. (649 g., 80%).

tert.-*Butylmalonic acid.* Ethyl *tert.*-butylmalonate (600 g., 2·8 moles) was hydrolyzed with absolute alcoholic potash solution as directed by Wideqvist, boiling under reflux being for 23 hr. The deliquescent potassium salt which had deposited was filtered off and washed with absolute alcohol (2 × 600 c.c.), and the bulk of adhering solvent removed over sulphuric acid *in vacuo*. The dried salt was dissolved in water (3 l.) and treated during 45 min. at <30° with 98% sulphuric acid (333 g., 3·3 moles) with good stirring. Butylmalonic acid was extracted with ether (3 × 500 c.c.). Removal of solvent and desiccation of the crystalline residue to constant weight *in vacuo* over sulphuric acid gave *tert.*-butylmalonic acid (346 g.). A further 8 g. of the acid was obtained by extracting the mixture again with ether (500 c.c.). Titration with sodium hydroxide (phenolphthalein) indicated 99·8% purity (79% yield, calc. on ethyl *tert.*-butylmalonate).

α-tert.-*Butylacrylic acid.* *tert.*-Butylmalonic acid (320 g., 2·0 moles) was stirred and cooled below 30° whilst aqueous dimethylamine (25·4 g./100 c.c.; 350 c.c., 2 moles) was added. Formaldehyde solution (35·5%; 169 g., 2 moles) was stirred into the crystalline paste at <20°. The mixture, now liquid, was kept at 20° for 6½ hr. (no evolution of carbon dioxide), then boiled under reflux for 6½ hr. Gas evolution commenced at 60°, and diminished gradually. The cooled product was acidified at <30° with 98% sulphuric acid (110 g., 1·1 mole), and the clear homogeneous liquid treated with water (1 l.). Rapidly crystallizing oil was precipitated. The mixture was extracted with light petroleum (b. p. 40—60°; 2 × 500 c.c.). The dried ($Na_2SO_4$) extracts left crude butylacrylic acid (62 g.) after removal of solvent and desiccation *in vacuo* over calcium chloride and active charcoal. Further extraction with light petroleum gave an additional 1 g. of acid. The crude butylacrylic acid was contaminated with *tert.*-butylacetic acid derived by decarboxylation of *tert.*-butylmalonic acid which had not undergone the Mannich reaction. Pure α-tert.-*butylacrylic acid*, obtained by recrystallization from warm light petroleum (b. p. 40—60°) in which, however, it is very soluble, had m. p. 44—44·5° (Found : C, 65·2; H, 9·5%; acid value, 437. $C_7H_{12}O_2$ requires C, 65·6; H, 9·5%; acid value, 438).

*tert.*-Butylmalonic acid (206 g.; 97·2% pure) was recovered from the reaction mixture by extraction with ether (2 × 350 c.c.).

*Oxidation of* α-tert.-*Butylacrylic Acid.*—The acid (2·6 g., 0·02 mole) was warmed above its m. p. with potassium hydroxide (1·2 g.) in water (400 c.c.). After cooling to 21°, potassium permanganate (6·3 g., 3 O) was added in portions during 6 min., with stirring. Reduction was rapid. This stage of the oxidation corresponded to conversion of the butylacrylic acid into *tert.*-butyltartronic acid. Further permanganate (4·2 g., 2 O) was then added, and the mixture warmed at 90° for 18 hr. Slow reduction, presumably after decarboxylation of the tartronic acid, was by then complete. Manganese dioxide was filtered off, and washed with water. Filtrate and washings were evaporated to about 25 c.c. on the water-bath, cooled, and treated with hydrochloric acid (10 ml.; *d* 1·18). Trimethylacetic acid which appeared was extracted with light petroleum (b. p. 40—60°). The petroleum extract was neutralized (phenolphthalein) with N-sodium hydroxide (17·4 c.c.; 87% of theory). The solution of sodium salt was concentrated and converted into the *p*-bromo- and *p*-phenyl-phenacyl ester. The esters, recrystallized from 95% alcohol, had (*p*-bromo), m. p. 77·5—78° (Found : Br, 26·9. Calc. for $C_{13}H_{15}O_3Br$: Br, 26·8%), and (*p*-phenyl), m. p. 113—113·5°. Authentic samples of the trimethylacetic esters had m. p.s 77·5—78·5° and 113·5—114° respectively.

*Methyl* α-tert.-*Butylacrylate.*—Crude α-*tert.*-butylacrylic acid (49 g.), methanol (75 g.), and sulphuric acid (1 g.) were boiled under reflux for 18 hr. Excess of methanol was distilled off through an 18″ Vigreux column (10 : 1 reflux ratio), the residue treated with an equal volume of water, and made alkaline with sodium hydroxide solution, and ester extracted with ether. The dried ($Na_2SO_4$) extract left crude ester (21·4 g.) on removal of solvent. Butylacrylic acid (30 g.) was recovered by acidification of the alkaline wash-liquid, extraction with ether, drying ($Na_2SO_4$), and removal of solvent. This recovered acid, esterified as above, gave further crude ester (15·2 g.) and recovered acid (8·1 g.). Crude ester (35·4 g.) was twice fractionally distilled, through a 6″ Dixon column (*J. Soc. Chem. Ind.*, 1949, **68**, 299), with a 30 : 1 reflux ratio, and gave methyl *tert.*-butylacetate, b. p. 128—130°/759 mm. (3·6 g.), and *methyl* α-tert.-*butylacrylate*, b. p. 145—146°/757 mm. (10·6 g.). By use of a 50-cm. column (1·0-cm. bore), packed with

Podbielniak " Heli-pak " No. 2916 flattened metallic spirals, crude ester (52·0 g.) gave in one pass methyl α-*tert.*-butylacrylate (37 g.) with methyl *tert.*-butylacetate (4·0 g.).

Methyl α-*tert.*-butylacrylate had b. p. 146—146·5°, $n_D^{20}$ 1·4272, $d_4^{20}$ 0·9033, $[R_L]_D$ 40·41 (Calc. : 40·33) [Found : C, 67·6; H, 9·6%; *M* (micro-vaporimetric), 140. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%; *M*, 142]. Methyl 2 : 2 : 3-trimethylbut-3-enoate obtained from methyl tetramethyllactate had $n_D^{20}$ 1·4288, $d_4^{20}$ 0·9126. Hydrogenation of the butylacrylate with Adams's catalyst (micro-method of Clauson-Kaas and Limborg, *Acta Chem. Scand.*, 1948, **1**, 884) showed 0·99 double bond.

*Polymerizability of Methyl* α-tert.-*Butylacrylate.*—(*a*) Ester (0·5 g.), containing benzoyl peroxide (5·6 mg.) in solution, was evacuated in a tube, cooled to −75°, and sealed. The tube was heated for 21 hr. at 85° without visible change. The product was evaporated at 15 mm. from a retort-shaped bulb of 25-c.c. capacity, immersed in a water-bath raised gradually to 100° and kept at 100° for 50 min. The wt. of residue, corrected for benzoyl peroxide, was 3% of the ester taken; it was a clear, colourless syrup, soluble immediately in cold light petroleum (b. p. 40—60°).

(*b*) Ester (6 c.c.) was irradiated for 213 hr. in a borosilicate tube with ultra-violet radiation, as described in Part I (*loc. cit.*). The appearance, viscosity, and refractive index ($\eta_D^{20}$ 1·0 c. p.; $n_D^{20}$ 1·4272) were unchanged. Evaporation of the irradiated ester as in (*a*) left 0·09% of residue after 60 min.' heating at 100°. Methyl methacrylate exposed simultaneously was converted into solid resin within 42 hr.

(*c*) Ester (4 g.) was treated with a solution of sodium (0·1 g.) in liquid ammonia (25 c.c.) at −75°, as described in Part I. The product was evaporated as in (*a*) (100°, 62 min., 9—10 mm.). The distillate had $n_D^{20}$ 1·4272. A liquid residue of *methyl* α*δ-di*-tert.-*butyladipate*, readily soluble in cold light petroleum (b. p. 40—60°), amounted to 29·9% of the ester taken [Found : C, 67·4; H, 10·5%; *M* (cryoscopic in benzene), 283. $C_{16}H_{30}O_4$ requires C, 67·1; H, 10·6%; *M*, 286].

(*d*) Ester (20 g.) was added to a stirred solution of sodium (1·62 g.) in liquid ammonia (150 c.c.) at −75°. During the addition (4 min.) the blue colour of the sodium solution changed to green, which was not replaced by the yellow sodium amide colour until about 1 min. after the addition. Yellowish solid was formed. After 30 min. at −75°, ammonium chloride (5 g.) was added. The yellow colour disappeared at once. The mixture was allowed to warm to room temperature, and treated with water (25 c.c.). The solid dissolved and an upper oily layer (19·5 g.) separated. The oil was washed with water, dilute hydrochloric acid, and water, and dried ($CaCl_2$), and distilled on a water-bath for 1 hr. at 27 mm. The distillate, redistilled, boiled at 145—147° and had $n_D^{20}$ 1·4270. Catalytic hydrogenation of this recovered methyl butylacrylate showed 0·98 double bond per molecule. The residual dimer (11·4 g.) had *M*, 259 (cryoscopic in benzene). It was distilled; after removal of some methyl butylacrylate, it passed over at 77°/0·04 mm. The colourless liquid had $n_D^{20}$ 1·4530, and did not take up hydrogen in presence of Adams's catalyst [Found : C, 67·1; H, 10·5%; *M* (cryoscopic in benzene), 284].

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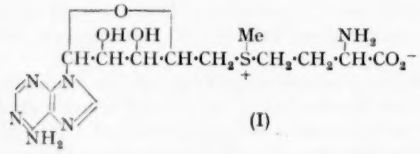
## 543. *Structural Observations on "Active Methionine."*

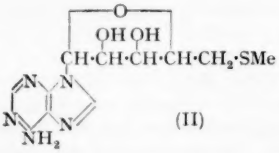
By J. Baddiley, G. L. Cantoni, and G. A. Jamieson.

The intermediate substance, "active methionine," which participates in the enzymic transfer of a methyl group from methionine to a variety of substrates has been hydrolysed to 5′-deoxy-5′-methylthioadenosine. This and other evidence confirms its formulation as *S*-(5′-deoxyadenosine-5′)-methionine.

The methyl group in methionine is readily transferred to other substances by enzymic processes in biological systems. In normal cells a stable dynamic state is achieved whereby continuous interchange of methyl groups occurs. However, such transmethylations involving methionine require the presence of adenosine triphosphate (ATP) (Borsook and Dubnoff, *J. Biol. Chem.*, 1947, **171**, 363; Cantoni, *ibid.*, 1951, **189**, 203; Cohen, *ibid.*, 1951, **193**, 851) and it has been shown recently that an intermediate substance, "active methionine" is formed (Cantoni, *ibid.*, 1951, **189**, 745). This unstable intermediate does not contain phosphorus and gives, after acid hydrolysis at 100°, adenine, homoserine, and an unidentified sulphur-containing compound (Cantoni, *J. Amer. Chem. Soc.*, 1952, **74**, 2942; *J. Biol. Chem.*, 1953, in the press). On the basis of this evidence "active methionine" has been formulated tentatively as *S*-(5′-deoxyadenosine-5′)-methionine (I).



(I)



(II)

Sulphonium compounds have hitherto been encountered only infrequently in Nature and, since the mechanism for the formation of (I) from ATP presents unusual features, further degradative evidence for the proposed structure was desirable. Sulphonium compounds decompose under a variety of conditions giving sulphides. The sulphides which could be formed theoretically from (I) are methionine, *S*-(5′-deoxyadenosine-5′)-homocysteine and 5′-deoxy-5′-methylthioadenosine ("adenine thiomethyl pentoside") (II). If (I) correctly represents "active methionine" it may be presumed that *S*-(5′-deoxyadenosine-5′)-homocysteine is formed biologically. However, the earlier observation that homoserine was produced during chemical hydrolysis suggested that the most vulnerable point of chemical attack on "active methionine" was the bond between the sulphur atom and the carbon chain of the amino-acid residue. Consequently, very cautious hydrolysis should yield 5′-deoxy-5′-methylthioadenosine (II). This has been shown to be the case. When a sample of "active methionine" was kept in the freeze-dried state at room temperature for a few weeks and then examined by paper chromatography the original spot had disappeared and a new spot was observed which absorbed ultra-violet light strongly and gave a negative ninhydrin reaction, and a positive aldehyde colour reaction after spraying of the paper with periodate according to the method of Buchanan, Dekker, and Long (*J.*, 1950, 3162). In all these respects it was indistinguishable from a synthetic sample of 5′-deoxy-5′-methylthioadenosine (Baddiley, *J.*, 1951, 1348; Weygand and Trauth, *Chem. Ber.*, 1951, **84**, 633; Satoh and Makino, *Nature*, 1951, **167**, 238). A larger sample of "active methionine" was heated at 100° in an acetate buffer at pH 7 whereupon crystalline 5′-deoxy-5′-methylthioadenosine was isolated. Small amounts of adenine were produced under these conditions but no adenosine or *S*-(5′-deoxyadenosine-5′)-homocysteine were observed.

The ready conversion of "active methionine" into (II) confirms formula (I) and establishes beyond doubt the biological origin of "adenine thiomethyl pentoside." Although the 5′-methylthio-compound was first isolated from yeast in 1912 (Mandel and Dunham, *J.*

*Biol. Chem.*, 1912, **11**, 85), only recently has it been established that its formation by micro-organisms depends on a good supply of methionine in the medium (Weygand, Junk, and Leber, *Z. physiol. Chem.*, 1952, **291**, 191; Smith and Schlenk, *Arch. Biochem.*, 1952, **38**, 167). The suggestion (Weygand, Junk, and Leber, *loc. cit.*) that it may arise from "active methionine" is confirmed by our findings. Furthermore, its presence in extracts of biological origin (cf. Smith, Anderson, Overland, and Schlenk, *Arch. Biochem.*, 1953, **42**, 72) should probably be attributed to chemical, rather than enzymic, decomposition of "active methionine" in the course of the procedure employed for the isolation of the 5′-methylthio-compound.

The conversion of "active methionine" into (II) may be followed by the accompanying decrease in the Bial orcinol test for pentose, owing to the fact that "active methionine" behaves in this test in a manner similar to adenosine, whereas (II) yields only 31·6% and 46·5%, respectively, of the colour (mole for mole) after 40 and 80 min.' heating at 100°.

The behaviour of "active methionine" on paper chromatography and its reaction on the paper are also consistent with formula (I). It moves very slowly in predominantly organic solvent mixtures and rapidly in salt solutions. It absorbs ultra-violet light, and gives a positive ninhydrin reaction and a purple colour after oxidation with periodate and spraying of the paper with Schiff's reagent (Buchanan, Dekker, and Long, *loc. cit.*). The ready production of an aldehyde in this test indicates the absence of substituents at positions 2′ and 3′ in the adenosine residue.

The presence of a strong positive charge on "active methionine" is seen from its rapid movement towards the cathode on paper electrophoresis. This probably is the most conclusive evidence for the presence of a sulphonium grouping in the molecule.

## Experimental

*Chromatographic Examination of "Active Methionine" Concentrate.*—Portions (0·005 c.c.) of an "active methionine" concentrate [containing *ca.* 100 micromoles/c.c. of "active methionine" (Cantoni, *J. Biol. Chem.*, 1951, **189**, 745)] were chromatographed on Whatman No. 4 filter paper with (*a*) ethanol–acetic acid–water (16 : 1 : 3), (*b*) 5% sodium dihydrogen phosphate solution, or (*c*) 5% ammonium sulphate solution covered with a surface layer of amyl alcohol.

$R_F$ values varied within small limits owing to lack of temperature control, and those tabulated below for room temperature (*ca.* 20°) are averages for several runs. Adenine derivatives were detected by their fluorescence in ultra-violet light. The ninhydrin and periodate–Schiff reactions were used as diagnostic sprays. In addition to "active methionine" and a little 5′-deoxy-5′-methylthioadenosine, a trace of methionine was present in the concentrate.

| | $R_F$ | | |
|---|---|---|---|
| | EtOH–AcOH–$H_2O$ | 5% $Na_2HPO_4$ | 5% $(NH_4)_2SO_4$ |
| "Active methionine" ..... | 0·14 | 0·73 | 0·73 |
| 5′-Deoxy-5′-methylthioadenosine ... | 0·57 | 0·58 | 0·58 |

*Hydrolysis.*—"Active methionine" concentrate (0·5 c.c.) was heated in a sealed tube for 48 hr. at 100°. Crystalline material was removed by filtration, then recrystallised twice from water; it had m. p. 205° (Kofler block), undepressed in admixture with a synthetic sample of 5′-deoxy-5′-methylthioadenosine. The two compounds were indistinguishable on chromatography in 5% sodium dihydrogen phosphate and in 5% ammonium sulphate solution.

*Electrophoresis.*—The cell employed was similar to that described by Markham and Smith (*Nature*, 1951, **168**, 406). Whatman No. 4 filter paper was soaked in an ammonium acetate buffer (pH 7), and the sample introduced at the centre of the strip. A potential of 200 v (D.C.) was applied for approx. 3 hr.; then the paper was examined in ultra-violet light. The spot observed for "active methionine" gave a positive ninhydrin test. The rates of progression towards the cathode were: "active methionine" 0·2; 5′-deoxy-5′-methylthioadenosine 0·07 cm. hr.$^{-1}$/v cm.$^{-1}$.

*Colorimetric Tests.*—A solution (2 c.c.) containing the nucleoside was placed in a Pyrex test-tube, and an equal volume of the orcinol–ferric chloride–hydrochloric acid reagent was added (Mejbaum, *Z. physiol. Chem.*, 1939, **258**, 117). The colour which developed after 40 and

80 min.' heating in a boiling-water bath was measured at 660 mμ and related to the adenine content as determined by the absorption at 260 mμ (molar extinction coefficient: 16,000).

| Compound | Adenine (micromole) | Pentose (micromole) | | | |
|---|---|---|---|---|---|
| | | 40 Min.* | 80 Min.* | | |
| | *a* | *b* | *c* | *c*/*b* | *b*/*a* |
| Adenosine | 0·0234 | 0·0234 | 0·0230 | 0·98 | 1·0 |
| Active methionine | 0·0334 | 0·0360 | 0·0402 | 1·11 | 1·07 |
| Active methionine (after hydrolysis at pH 6·4 and 100° for 4 hr.) | 0·0427 | 0·0218 | 0·0263 | 1·21 | 0·51 |
| Active methionine (after hydrolysis at pH 6·4 and 100° for 10 hr.) | 0·0427 | 0·0173 | 0·0220 | 1·27 | 0·405 |
| (II) | 0·060 | 0·019 | 0·0278 | 1·46 | 0·316 |

* Heating time at 100°.

Quantitative chromatographic analysis of the solutions of "active methionine" used in this experiment (for technical details, see Cantoni, *J. Biol. Chem.*, 1953, in the press) confirmed the disappearance of "active methionine" on hydrolysis and concomitant formation of 5'-deoxy-5'-methylthioadenosine. Thus, before hydrolysis of the total adenine-containing compounds, 84% was identical with (I) and 16% migrated as (II). After 4 hr.' hydrolysis, the figures were 12% and 88%, respectively.

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## 544. *Syntheses in the Morphine Series. Part V.* Model Experiments for the Introduction of Oxygen at* $C_{(6)}$.

By Dov Elad and David Ginsburg.

In the substituted *cyclo*hexanones and octahydro-oxophenanthrenes investigated, the most efficient method for introduction of a carbonyl group α to an existing one is an indirect one, through preparation of the α-hydroxyimino-ketones.

Attempted conversion of the stable methyl *trans*-3-oxo-2-phenyl*cyclo*hexylacetate and *trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-4-oxophenanthrene into the corresponding *cis*-isomers, by halogenation, dehydrohalogenation, and hydrogenation, failed.

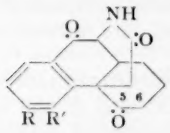
In Part IV * the synthesis of a tetracyclic compound (I*a*) was described. This substance bears an oxygen function at $C_{(5)}$ which can be used as a key to ring C of morphine (II). It is necessary first to introduce an oxygen atom at $C_{(6)}$ as this position bears a hydroxyl group in morphine itself. Subsequently, the 5-oxygen atom in a substance such as (I*b*) can be removed with a view to obtaining dihydrothebainone as the final product in the reaction sequence. Alternatively, the 5-oxygen atom can be utilised together with the 4-methoxy group with a view to obtaining dihydrocodeinone as the ultimate product. The best means for accomplishing the oxygenation of $C_{(6)}$, therefore, assumes paramount importance in our route of morphine synthesis. In this communication, experiments with model compounds to this end are described.

The substance chosen as the simplest model for the system under investigation was 2-phenyl*cyclo*hexanone. Oxidation of this ketone with selenium dioxide, as in the similar oxidation of 2-methyl*cyclo*hexanone (Godchot and Cauquil, *Compt. rend.*, 1936, **202**, 326), yielded, as the major product, 2-phenyl*cyclo*hex-2-enone identical with the compound described by Ginsburg and Pappo (*J.*, 1951, 516). Although a small amount of the desired

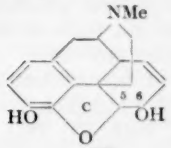
* Part IV, *J.*, 1953, 1524.

diketone was present in the reaction mixture, as shown by the strongly positive ferric chloride test, this route was clearly inefficient.

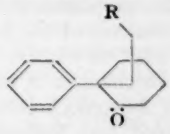
In order to avoid the difficulties inherent in substances containing a tertiary hydrogen atom adjacent to a carbonyl group, models were chosen in which this hydrogen atom was



(I*a*; R = R′ = H)
(I*b*; R = R′ = OMe)



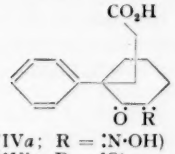
(II)



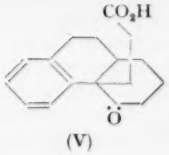
(III*a*; R = $CO_2H$)
(III*b*; R = CN)
(III*c*; R = $CO_2Me$)

replaced by a substituted alkyl group, *e.g.*, (III*a*, *b*, c), obtained by cyanoethylation, etc., of 2-phenyl*cyclo*hexanone (Bachmann and Wick, *J. Amer. Chem. Soc.*, **1950**, **72**, 3388). Bromination of these substances with bromine or with *N*-bromosuccinimide gave the 6-bromo-derivatives. Attempted conversion of these α-bromo-ketones into the corresponding ketols under a large variety of reaction conditions failed (see Experimental section). In most cases the starting material was recovered unchanged. The difficulty in removing the $C_{(6)}$ bromine atom under $S_N1$ displacement conditions may be explained by the simple electromeric effect operating in the attempted removal as bromide ion of a bromine atom α to a carbonyl group. A study of models shows that irrespective of whether one places the phenyl group or the β-substituted ethyl group at $C_{(2)}$ in the polar or in the equatorial conformation, either in the chair or in the boat form of the *cyclo*hexane ring, an equatorial bromine atom at $C_{(6)}$ is sterically hindered with respect to approach from the rear ($S_N2$). Since one would expect the bulky bromine atom to assume the equatorial conformation in preference to the polar, this subtle steric effect may be responsible for the sluggishness of the bromine atom under $S_N2$ conditions also.

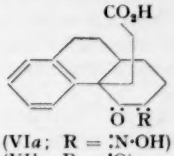
The next method employed involved indirect oxygenation at the α-carbon atom through preparation of the α-hydroxyimino-ketone, with subsequent hydrolysis to the β-diketone. Indeed, this proved to be the method of choice and appeared to solve the problem also insofar as yield was concerned. When (III*a*) is treated with *n*-amyl nitrite in the presence of sodium ethoxide, the α-hydroxyimino-ketone (IV*a*) is obtained in 93% yield. When acid catalysis was employed, a very low yield of this substance was obtained. It was hydrolysed by two methods described by Barltrop, Johnson, and Meakins (*J.*, 1951, 181) to the desired β-diketone (IV*b*). Treatment of (IV*a*) with zinc and acetic acid did not give



(IV*a*; R = :N·OH)
(IV*b*; R = :O)



(V)



(VI*a*; R = :N·OH)
(VI*b*; R = :O)

the expected ketol; reversal of the hydroximination reaction took place and (III*a*) was isolated in low yield (cf. Caunt, Crow, Haworth, and Vodoz, *J.*, 1950, 1631).

In order to approach more closely the system of primary interest in this work, 12-2′-carboxyethyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-4-oxophenanthrene (V) (Part IV) was used as a model substance. The α-hydroxyimino-ketone (VI*a*) was obtained in 90% yield under alkali-catalysed conditions. Transoximation with formaldehyde–hydrochloric acid yielded the desired αβ-diketone (VI*b*).

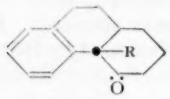
Clearly, the introduction of the oxime group α to the carbonyl group in these compounds is possible only because $C_{(2)}$ in 2-phenyl*cyclo*hexanone and $C_{(12)}$ in the octahydrophenanthrene derivative are quaternary. It is well known that cleavage of the molecule takes place by attack of a nitroso-ion on a tertiary carbon atom, with the formation of the oximes of the keto-acids or keto-esters which result from such cleavage.

This cleavage reaction has been used extensively (cf. Lapworth and Wechsler, *J.*, **1907**, **91**, 977, 1919; Woodward and Doering, *J. Amer. Chem. Soc.*, **1945**, **67**, 860).

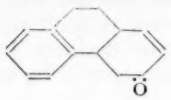
Thus, treatment of 2-phenyl*cyclo*hexanone with *n*-amyl nitrite in the presence of sodium ethoxide gave in high yield the oxime of δ-benzoylvaleric acid. Similarly, the octahydro-oxophenanthrene (VII*a*) yielded γ-(1-hydroxyimino-2-tetralyl)butyric acid. The derivatives of the keto-acids, and not those of the keto-esters, were isolated because Claisen solution was used in the isolation procedure.

The mechanism of the formation of *hetero*cholestenone by the high-temperature treatment of 2-bromocholestan-3-one with potassium acetate in acetic acid is still obscure (Butenandt and Ruhenstroth, *Ber.*, **1944**, **77**, 397). This rearrangement involves the conversion of the system ·CHBr·CO·$CH_2$·CH·$CH_2$· into ·$CH_2$·$CH_2$·CO·C:CH· with the loss of one mol. of hydrogen bromide. It seemed of interest, purely on grounds of analogy, to investigate whether in one of the systems of interest in morphine synthesis, it would be possible to carry out a similar rearrangement (VII*b* ⟶ VIII). If this rearrangement could be carried out, one would have a novel method for oxygenation at $C_{(6)}$. Further, a substance such as (VIII) could be reduced and used as a model for solving other points, the knowledge of which is required in the problem of morphine synthesis. Thus, for example, it might be expected that bromination of the dihydro-derivative of (VIII) would take place at $C_{(4)}$, by analogy with the bromination of 3-phenyl*cyclo*hexanone at $C_{(2)}$. The latter point was proved by dehydrobromination to 3-phenyl*cyclo*hex-2-enone identical with the product described by Abdullah (*J. Ind. Chem. Soc.*, **1935**, **12**, 62).

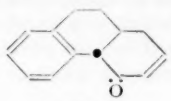
Bromination of (VII*a*) in carbon tetrachloride (cf. Bachmann and Wick, *loc. cit.*, for the similar bromination of 2-phenyl*cyclo*hexanone) yields the 12-bromo-derivative (VII*b*). Heating the latter with potassium acetate–acetic acid at 200° yields an αβ-ethylenic ketone (IX). Since reduction of (IX) yields (VII*a*), the desired rearrangement did not take place. Dehydrobromination of (VII*b*) by lutidine or 2 : 4-dinitrophenylhydrazone yields a different αβ-ethylenic ketone (X), which on catalytic hydrogenation also leads to the starting material (VII*a*). Isolation of two 2 : 4-dinitrophenylhydrazones in the latter reaction pointed to the possibility that a mixture of (VII*a*) and the *cis*-ketone (XI) had been obtained, but in view of experience in a similar reaction sequence employing methyl 3-oxo-2-phenyl*cyclo*hexylacetate, this possibility seemed remote (see below). Indeed, it



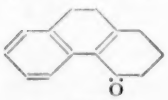

(VII*a*; R = H)
(VII*b*; R = Br)



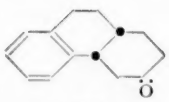

(VIII)



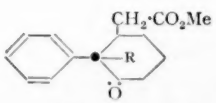

(IX)




(X)




(XI)




(XII*a*; R = H)
(XII*b*; R = Br)
(XII*c*; R = Cl)

was shown that the formation of a mixture of two 2 : 4-dinitrophenylhydrazones could be controlled by means of the amount of acid in the 2 : 4-dinitrophenylhydrazine solution employed and that the low-melting form could be converted into the high-melting form by means of acid; they may be the *syn*- and the *anti*-form, respectively, of the 2 : 4-dinitrophenylhydrazone. However, both forms are derivatives of the *trans*-octahydro-oxophenanthrene (VII*a*), as mixtures of them could be obtained directly from pure (VII*a*) which was not put through the bromination–dehydrobromination–hydrogenation sequence.

The greater stability of the *trans*-ketone (VII*a*), compared with that of the still unknown *cis*-isomer (XI), is paralleled also in the substituted *cyclo*hexanone series. Bromination or chlorination of methyl 3-oxo-2-phenyl*cyclo*hexylacetate (XII*a*) yields (XII*b* and *c*,

respectively). Dehydrohalogenation of the halides, followed by catalytic hydrogenation, affords only the *trans*-product (XII*a*).

## Experimental

*Selenium Dioxide Oxidation of* 2-*Phenyl*cyclo*hexanone*.—To a boiling solution of 2-phenyl-*cyclo*hexanone (8·7 g.) in absolute ethanol (25 ml.) a solution of sublimed selenium dioxide (5·5 g.) in absolute ethanol (30 ml.) was added dropwise during 1 hr. The mixture was heated under reflux for 6 hr., the precipitated selenium was removed by filtration, and the solvent removed under reduced pressure. The residue was extracted with ether, filtered, and fractionated. The first fraction, b. p. 135—140°/3 mm. (2·2 g.), m. p. 97° (from heptane), showed no m. p. depression upon admixture with authentic 2-phenyl*cyclo*hex-2-enone. A further crop of this ketone could be obtained from the higher-boiling fraction. The mother-liquor gave an intense colour with alcoholic ferric chloride.

*Reaction of* 2-*Phenyl*cyclo*hexanone with* n-*Amyl Nitrite*.—To a solution of sodium ethoxide (1·27 g. of sodium in 25 ml. of absolute ethanol) were added 2-phenyl*cyclo*hexanone (8·7 g.) and, with ice-cooling, *n*-amyl nitrite (8·8 ml.). The mixture became homogeneous after several hours and was kept in the refrigerator for 48 hr. Acetic acid (10 ml.) and a large volume of water were added, the mixture was extracted twice with ether, and the combined ethereal extracts were shaken twice with Claisen solution. The alkaline solution was acidified with acetic acid and diluted with water. After refrigeration, the solution deposited colourless crystals, m. p. 119—120° (from aqueous ethanol), of the *oxime* of δ-benzoylvaleric acid (5·6 g.). The filtrate was extracted with ether, the solvent was removed, and the residue furnished an additional crop of product (1·4 g.; total yield 67%) (Found: C, 65·8; H, 6·8; N, 6·4. $C_{12}H_{15}O_3N$ requires C, 65·1; H, 6·8; N, 6·3%).

Hydrolysis of the oxime with dilute hydrochloric acid, containing a small amount of ethanol to give a homogeneous solution, yielded δ-benzoylvaleric acid, m. p. 78—79° (from aqueous ethanol). The semicarbazone, prepared in pyridine, had m. p. 186—187° (from aqueous ethanol). Von Auwers and Treppmann (*Ber.*, 1915, **48**, 1217) reported m. p.s 77—78° and 187°, respectively, for these substances.

2-2′-*Carboxyethyl*-6-*hydroxyimino*-2-*phenyl*cyclo*hexanone*.—To an ice-cold solution of sodium ethoxide (from 0·5 g. of sodium and 10 ml. of ethanol) were added 2-2′-carboxyethyl-2-phenyl-*cyclo*hexanone (2·5 g.) and *n*-amyl nitrite (1·8 ml.). The orange mixture was kept in the refrigerator for 48 hr. and then treated as above, except that sodium hydrogen carbonate was used instead of Claisen solution. The *hydroxyimino-acid* was obtained as cream-coloured crystals, m. p. 168—169° (decomp.). Recrystallisation from aqueous ethanol raised the m. p. to 174° (decomp.). The substance gives a green colour with alcoholic ferric chloride (Found: C, 65·7; H, 6·2; N, 5·3. $C_{15}H_{17}O_4N$ requires C, 65·4; H, 6·2; N, 5·1%).

2-2′-*Carboxyethyl*-6-*oxo*-2-*phenyl*cyclo*hexanone*.—(*a*) The hydroxyimino-compound (0·2 g.), formaldehyde solution (40%; 1 ml.), and hydrochloric acid (2N; 0·2 ml.) were heated on the steam-bath for 10 min. Water (10 ml.) was added to the resulting yellow solution and the precipitated oil was taken up in ether. The ethereal extract was washed with water, the ether removed, and the remaining oil gave an intense brown colour with alcoholic ferric chloride. The product was not as pure as that obtained by method (*b*).

(*b*) To a solution of the hydroxyimino-ketone (1 g.) and sodium nitrite (2·4 g.) in 50% aqueous ethanol (400 ml.), concentrated sulphuric acid (2·4 ml.) was added dropwise with cooling. The mixture was kept at 35—40° for 36 hr. Sodium hydrogen carbonate solution was used to adjust the pH to 6 and the mixture was concentrated under reduced pressure to about half of its original volume. The oil which separated was extracted with ether, the ethereal extract washed with water, and the solvent removed. After several weeks, the *αβ-diketone* became semi-solid (Found: C, 69·4; H, 6·1. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%). It gave a deep brown colour with alcoholic ferric chloride.

6-*Bromo*-2-2′-*carboxyethyl*-2-*phenyl*cyclo*hexanone*.—To a boiling solution of (III*a*) (1·2 g.) in carbon tetrachloride (20 ml.) was added dropwise a solution of bromine (0·3 ml.) in carbon tetrachloride (10 ml.). The colour of the bromine disappeared immediately. After removal of the solvent under reduced pressure the remaining oil was crystallised from aqueous methanol or heptane. The colourless *bromo-acid* had m. p. 149—150°. Further recrystallisation raised the m. p. to 151—152° (Found: C, 55·4; H, 5·3; Br, 24·7. $C_{15}H_{17}O_3Br$ requires C, 55·4; H, 5·2; Br, 24·6%).

6-*Bromo*-2-2′-*cyanoethyl*-2-*phenyl*cyclo*hexanone*.—To a solution of (III*b*) (1·1 g.) in carbon tetrachloride (20 ml.) was added dropwise with cooling a solution of bromine (0·3 ml.) in carbon

tetrachloride (10 ml.). A heavy brown oil separated. The solvent was removed under reduced pressure and the oily residue was extracted twice with boiling heptane. Colourless crystals, m. p. 116—117°, of the *bromo-nitrile* were obtained from the heptane solution (Found: C, 56·7; H, 5·5; Br, 26·3. $C_{15}H_{16}ONBr$ requires C, 56·0; H, 5·2; Br, 26·2%).

The bromo-nitrile (1 g.), acetic acid (10 ml.), and hydrochloric acid (1 : 1; 10 ml.) were heated under reflux for 15 hr. under carbon dioxide, then poured into water and cooled. The precipitated bromo-acid was recrystallised from heptane and proved to be identical with the bromo-acid obtained by bromination of (III*a*).

6-*Bromo*-2-2′-*carbomethoxyethyl*-2-*phenyl*cyclo*hexanone*.—The ester (III*c*) (2·6 g.), *N*-bromosuccinimide (1·9 g.), and a trace of benzoyl peroxide were added to carbon tetrachloride (20 ml.), and the mixture was heated under reflux for 12 hr. The succinimide was removed by filtration and the solvent removed under reduced pressure. The resulting *bromo*-ester was an oil which did not crystallise. Hydrolysis of the bromo-ester as described above for the bromo-nitrile yielded the bromo-acid, m. p. 151—152°, identical with the bromination product of (III*a*).

Attempted displacement of the 6-bromine atom in the above substances failed under the following reaction conditions: silver nitrate–pyridine, silver acetate–benzene, potassium formate–methanol, aqueous potassium carbonate, potassium acetate–acetic acid. Further, neither lutidine nor 2 : 4-dinitrophenylhydrazine in acetic acid had any effect on the substances which were recovered unchanged even after long reflux periods.

*Methyl* 2-*Chloro*-3-*oxo*-2-*phenyl*cyclo*hexylacetate*.—To a solution of methyl 3-oxo-2-phenyl-*cyclo*hexylacetate (2·6 g.) in carbon tetrachloride (50 ml.) was added dropwise a solution of sulphuryl chloride (1·5 g.) in carbon tetrachloride (10 ml.). The mixture was refluxed for 2 hr. There was then no further evolution of sulphur dioxide and hydrogen chloride. The solvent was removed under reduced pressure and the residue was triturated with light petroleum. After recrystallisation of the colourless solid (2·5 g.), the *chloro*-derivative had m. p. 111—112° (from light petroleum) (Found: C, 64·1; H, 6·1; Cl, 12·6. $C_{15}H_{17}O_3Cl$ requires C, 64·2; H, 6·1; Cl, 12·7%).

Dehydrochlorination with 2 : 6-lutidine gave an oil whose 2 : 4-dinitrophenylhydrazone had m. p. 112—113° (from ethanol). Hydrogenation of the oil in ethanol with 10% palladised charcoal at an initial pressure of 60 lb./sq. in. gave methyl *trans*-3-oxo-2-phenyl*cyclo*hexylacetate, m. p. and mixed m. p. 81° (from methyl*cyclo*hexane).

*Methyl* 2-*Bromo*-3-*oxo*-2-*phenyl*cyclo*hexylacetate*.—(*a*) To a solution of methyl 3-oxo-2-phenyl*cyclo*hexylacetate (5·7 g.) in carbon tetrachloride (60 ml.) was added at 0—5° a solution of bromine (1·2 ml.) in carbon tetrachloride (20 ml.). A brown oil separated at the end of the rapid addition. The solvent was removed under reduced pressure and the residue triturated with methanol. The *bromo*-ester (6·2 g.) had m. p. 131—132° (from hexane) (Found: C, 55·8; H, 5·4; Br, 24·4. $C_{15}H_{17}O_3Br$ requires C, 55·4; H, 5·2; Br, 24·6%).

(*b*) A mixture of methyl ester (5·15 g.), *N*-bromosuccinimide (3·72 g.), and carbon tetrachloride (50 ml.) was heated on the steam-bath for 30 min. Since no apparent reaction had taken place, a trace of benzoyl peroxide was added. After 45 min.' additional boiling, all the *N*-bromosuccinimide had been replaced by succinimide which was removed by filtration. The solvent was removed under reduced pressure and the residue treated as above, m. p. 131—132° (5·2 g.). On admixture with the product obtained by method (*a*) there was no m. p. depression.

Dehydrobromination was accomplished by 1 hr.' heating with 2 : 6-lutidine. After the usual working up an oily unsaturated ester was obtained which gave the same 2 : 4-dinitrophenylhydrazone, m. p. 112—113°, as was obtained from the above chloro-ester. Hydrogenation of the unsaturated ester in ethanol in the presence of 10% palladised charcoal at an initial pressure of 60 lb./sq. in. yielded authentic methyl *trans*-3-oxo-2-phenyl*cyclo*hexylacetate, m. p. and mixed m. p. 81°. No isomeric ester could be isolated.

*Bromination of* 3-*Phenyl*cyclo*hexanone*.—A mixture of 3-phenyl*cyclo*hexanone (2·2 g.), *N*-bromosuccinimide (1·9 g.), and carbon tetrachloride (20 ml.) was heated under reflux for 2 hr. Hydrogen bromide was evolved during this time. The succinimide was removed, the solvent evaporated under reduced pressure, and the residue heated with 2 : 6-lutidine (20 ml.) for 2 hr. The lutidine was removed under reduced pressure, the residual oil dissolved in ether, and the extract washed with dilute hydrochloric acid and water. After removal of the ether, the residue was treated with ethanolic 2 : 4-dinitrophenylhydrazine. A deep red 2 : 4-dinitrophenylhydrazone (0·8 g.) was obtained, having m. p. 224—226° (from ethanol), identical with the 2 : 4-dinitrophenylhydrazone of 3-phenyl*cyclo*hex-2-enone (cf. Ginsburg and Pappo, *J.*, 1951, 516).

*Bromination of* 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro*-4-*oxophenanthrene*.—To the octahydro-oxophenanthrene (VII*a*) (2 g.) in carbon tetrachloride (20 ml.) was added with ice-cooling a solution of bromine (1·6 g.) in carbon tetrachloride (10 ml.). The colour of the bromine disappeared immediately. The solvent was removed under reduced pressure and the residual oil was essentially pure 12-*bromo*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-4-*oxophenanthrene* (VII*b*) (Found : Br, 28·9. $C_{14}H_{15}OBr$ requires Br, 28·7%). In one experiment, on treatment of the oil with hot butanol, a very small amount of solid, m. p. 118—120°, remained undissolved. This is probably the 3 : 12-*dibromo*-derivative (Found : Br, 44·4. $C_{14}H_{14}OBr_2$ requires Br, 44·7%).

*Dehydrobromination*.—(a) *With lutidine*. To the 12-bromo-compound (2·8 g.) was added 2 : 6-lutidine (20 ml.), and the solution refluxed for 2 hr. After the usual working up, the residual oily αβ-ethylenic ketone (X) was treated with 2 : 4-dinitrophenylhydrazine in ethanol. The 2 : 4-*dinitrophenylhydrazone* of 1 : 2 : 3 : 4 : 9 : 10-hexahydro-4-oxophenanthrene had m. p. 230—232° (from ethanol–chloroform) (Found : C, 63·4; H, 4·6; N, 14·8. $C_{20}H_{18}O_4N_4$ requires C, 63·5; H, 4·8; N, 14·8%); $\lambda_{max.}$ = 3930 Å; ε = 24,000 (in $CHCl_3$). It was unaccompanied by any isomeric hydrazone, as shown by attempted chromatographic separation on alumina.

When the 12-bromo-compound was treated directly with 2 : 4-dinitrophenylhydrazine in ethanol, the same 2 : 4-dinitrophenylhydrazone, m. p. 230—232°, was obtained, unaccompanied by any isomer.

(b) *With potassium acetate–acetic acid*. The 12-bromo-compound (VII*b*) (2·8 g.) and a solution of potassium acetate in acetic acid (21%; 85 ml.) were heated in a sealed tube at 200—210° for 5 hr. The mixture was poured into a large volume of water and extracted with ether, and the extract washed with 2N-potassium hydroxide until the aqueous layer remained alkaline. After evaporation of the ether, the residual oil was treated with ethanolic 2 : 4-dinitrophenylhydrazine. A mixture of 2 : 4-dinitrophenylhydrazones was obtained, separable by fractional crystallisation. The 2 : 4-*dinitrophenylhydrazone* of 1 : 4 : 9 : 10 : 11 : 12-hexahydro-4-oxophenanthrene (IX) was much less soluble and had m. p. 269—270° (from 1 : 1 ethanol–chloroform) (Found : C, 63·6; H, 4·7; N, 14·7. $C_{20}H_{18}O_4N_4$ requires C, 63·5; H, 4·8; N, 14·8%); $\lambda_{max.}$ 3970 Å; ε = 28,000 (in $CHCl_3$). The isomeric 2 : 4-dinitrophenylhydrazone, m. p. 230—232°, identical with the one described above could be obtained from the mother-liquor. Mixtures were always obtained by this dehydrobromination procedure, consisting of 50—80% of the higher-melting isomer.

*Hydrogenation of* αβ-*Ethylenic Ketones*.—Ketone (IX) or (X) (1 g.) was hydrogenated in ethanol (20 ml.) in the presence of 10% palladised charcoal (0·3 g.) at 60°, at an initial pressure of 60 lb./sq. in. After 2 hr., the catalyst was removed and the ethanol distilled under reduced pressure. The solution afforded a mixture of two 2 : 4-dinitrophenylhydrazones. The mixture was extracted with boiling methanol, and the methanolic solution was allowed to cool. A high-melting β-*form* was obtained as light orange rosettes, m. p. 217—218° (Found: C, 63·0; H, 5·0; N, 14·5. $C_{20}H_{20}O_4N_4$ requires C, 63·2; H, 5·3; N, 14·7%). The methanol-insoluble α-form was recrystallised from ethanol–chloroform and was obtained as yellow prismatic needles, m. p. 196°, identical with the compound described by Ginsburg and Pappo (*J.*, 1951, 938). When the low-melting form was dissolved in 1 : 1 ethanol–sulphuric acid, kept overnight, and then diluted with aqueous ethanol, a mixture was obtained containing an appreciable amount of the high-melting form. The α-form (196°) showed $\lambda_{max.}$ 3690 Å (ε = 24,000 in $CHCl_3$). The β-form (m. p. 217—218°) showed $\lambda_{max.}$ 3700 Å (ε = 23,000 in $CHCl_3$).

*Reaction of* (VII*a*) *with* n-*Amyl Nitrite*.—To a solution of sodium ethoxide (from 0·07 g. of sodium and 5 ml. of ethanol), were added (VII*a*) (0·6 g.) in ethanol (3 ml.) and *n*-amyl nitrite (0·5 g.), with ice-cooling. After being kept in the refrigerator for 48 hr., the mixture was treated as described for the similar reaction of 2-phenyl*cyclo*hexanone (see above). The *oxime*, m. p. 128—129°, of γ-(1 : 2 : 3 : 4-tetrahydro-1-oxo-2-naphthyl)butyric acid was obtained from aqueous ethanol (Found : C, 68·2; H, 6·9; N, 5·6. $C_{14}H_{17}O_3N$ requires C, 68·0; H, 6·9; N, 5·7%).

The same product can be obtained by use of *n*-butyl nitrite.

The free keto-acid, obtained by acid hydrolysis, had m. p. 64—65° (from heptane). Bachmann and Wendler (*J. Amer. Chem. Soc.*, 1946, **68**, 2580) reported m. p. 64—65°.

γ-2-*Naphthylbutyric Acid*.—The methyl ester of the above keto-acid was obtained by treating the keto-acid (600 mg.) with ethereal diazomethane. The ester was an oil whose 2 : 4-dinitrophenylhydrazone had m. p. 158—160° (from ethanol).

The crude methyl ester was treated in methanol (10 ml.) with sodium borohydride (100 mg.). After dilution with water and ether-extraction, the ether was removed and the crude reduction product heated in *p*-cymene with 10% palladised charcoal (0·5 g.) under reflux for

4 hr. (nitrogen). After cooling of the mixture, ether was added, the catalyst removed, and the ether evaporated. The residue was heated in methanolic potassium hydroxide (30%; 10 ml.) under reflux for 90 min. After dilution with water, acidification, and ether-extraction, the ether was washed with aqueous sodium hydrogen carbonate and the alkaline extract was acidified. The precipitate had m. p. 103—104° (from heptane). Newman and Zahm (*ibid.*, 1943, **65**, 1097) report m. p. 98—99° for γ-2-naphthylbutyric acid.

cis-12-2′-*Carboxyethyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-3-*hydroxyimino*-4-*oxophenanthrene* (VI*a*).—To an ice-cold solution of sodium ethoxide (from 0·25 g. of sodium and 5 ml. of ethanol) were added, with cooling, (V) (1·35 g.) and *n*-amyl nitrite (0·9 ml.). After several hours in the refrigerator all of the solid had dissolved and the orange solution was refrigerated for a total of 48 hr. After the usual working up the *hydroxyimino-oxo-acid* (VI*a*) (1·35 g., 90%) was obtained, having m. p. 204° (decomp.; sinters at 196°). An analytical sample was obtained by washing the precipitated product with ether (Found: C, 67·6; H, 6·3; N, 4·2. $C_{17}H_{19}O_4N$ requires C, 67·8; H, 6·4; N, 4·7%).

cis-12-2′-*Carboxyethyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro*-3 : 4-*dioxophenanthrene*.—The hydroxyimino-compound (VI*a*) (0·6 g.), formaldehyde solution (40%; 3 ml.), and hydrochloric acid (2N; 0·6 ml.) were heated on the steam-bath. After 6 min. all of the solid had dissolved and the light orange solution became turbid. After being heated for 4 additional min. the mixture was cooled and water (10 ml.) was added. After a further few minutes, the supernatant liquid was decanted from the precipitated oil, and the residue was extracted twice with boiling heptane containing a few drops of benzene. A solid, m. p. 124—127°, was precipitated from the organic extract. After four recrystallisations (charcoal) the *diketone* had m. p. 140—143° (from heptane) (yield, 35%) (Found: C, 71·5; H, 6·3. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%). The product gave a dark brown colour with alcoholic ferric chloride.

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## 545. *The Structure of Nickel Tetracarbonyl and Some Disubstituted Derivatives.*

By R. S. NYHOLM and L. N. SHORT.

The structure of nickel tetracarbonyl is discussed. The infra-red spectrum and bond-length data are shown to be more compatible with a structure involving four Ni–C double bonds than with the generally accepted structure of two double bonds resonating among four positions. The stretching force constants of the C–O bonds in two disubstituted nickel carbonyls (*o*-phenylenebisdimethylarsinedicarbonylnickel[0] and dipyridyldicarbonylnickel[0]) have been calculated from the infra-red frequencies. Consideration of these leads to the conclusion that the metal–ligand bonds in these complexes possess considerable double-bond character.

IN order to explain the properties of certain transition-metal complexes it has been suggested that metal–ligand bonds may possess double-bond character (see, *e.g.*, Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1948, 2nd edn., p. 250; Chatt, *Nature*, 1950, **165**, 637; *J.*, 1952, 4300; Nyholm, *J.*, 1952, 2906; and for more detailed references see Nyholm, *J.*, 1951, 3245). Direct physical evidence on the point is difficult to obtain, but it was thought that observation of the bond-stretching force constants of the carbonyl bonds remaining when one or more of the carbonyl groups in nickel tetracarbonyl are replaced by other ligands would probably allow the nature of the metal–ligand bond to be inferred.

The vibrational spectrum of nickel tetracarbonyl was studied by Crawford and Cross (*J. Chem. Phys.*, 1938, **6**, 525), who reported a value of $15{\cdot}89 \times 10^5$ dynes cm.$^{-1}$ for the carbonyl bond-stretching force constant; they concluded that, since this value lies between the values associated with the C–O double bond in formaldehyde ($12{\cdot}1 \times 10^5$) and the triple bond in carbon monoxide ($18{\cdot}6 \times 10^5$ dynes cm.$^{-1}$), the nickel tetracarbonyl C–O bonds have partial triple-bond character. The structure of this compound was regarded therefore as a resonance hybrid of structures such as (I). The fact that the carbonyl force

constants of nickel tetracarbonyl and carbon dioxide ($15{\cdot}5 \times 10^5$; Herzberg, " Infra-red and Raman Spectra," Van Nostrand, N.Y., 1945, p. 187) are very similar was also noted.

(I) (II)

The validity of comparison of the force constants of nickel tetracarbonyl and formaldehyde must be questioned, since the σ-bonds formed by the carbon atoms in those two cases are of different types. In formaldehyde the carbon bonds are $sp^2$ (trigonal) hybrids, while in nickel tetracarbonyl, for which the Ni–C–O groups are linear (Sutton, New, and Bentley, *J.*, 1933, 652; Ladell, Post, and Frankuchen, *Acta Cryst.*, 1952, **5**, 795), the carbon bonds are *sp* hybrids. It is known that increase in the proportion of *s* to *p* character in the carbon bonds is accompanied by an increase in bond strength (Sutherland and Dennison, *Proc. Roy. Soc.*, 1935, *A*, **148**, 250; Walsh, *J.*, 1948, 398; Maccoll, *Trans. Faraday Soc.*, 1950, **46**, 359).

Few compounds are available having a carbonyl group of which the carbon has *sp* hybridisation, and these are such that simple conclusions about their structure are difficult to reach. Carbon dioxide and carbonyl sulphide have C–O bond-stretching force constants of 15·5 and $14{\cdot}2 \times 10^5$ dynes cm.$^{-1}$, respectively (Herzberg, *op. cit.*, pp. 174, 187). Pauling (*op. cit.*, p. 197) has explained the bond lengths in these compounds as being due to resonance involving partial triple-bond character. If it be recognised that bond characteristics depend on the hybridisation of the σ-bonds involved, the importance of such resonance is much diminished. For example, a C–O bond length of about 1·15 Å and force constant of $15{\cdot}5 \times 10^5$ dynes cm.$^{-1}$ appear to be characteristic of a normal double bond involving *sp* hybrid σ-bonds. On this basis carbon dioxide may be represented satisfactorily as O=C=O (Coulson, " Valence," O.U.P., 1952, p. 211). A further example of this type of carbonyl bond is afforded by keten ($CH_2$=C=O) in which the C–O bond length is 1·17 Å (Beach and Stevenson, *J. Chem. Phys.*, 1938, **6**, 75). Halverson and Williams (*ibid.*, 1947, **15**, 552) give a set of force constants for keten including $15{\cdot}5 \times 10^5$ dynes cm.$^{-1}$ for the carbonyl bond stretching constant, which can be used to calculate the $A_1$ vibration frequencies to within 2%. However, since there are only four frequencies (*A* species) and at least five force constants, *viz.*, C=O stretching ($K_{C=O}$), C=C stretching ($K_{C=C}$), C–H stretching ($K_{C-H}$), $CH_2$ bending ($K_{\delta CH_2}$), and C=C=O interaction ($k$), are required for a reasonable representation of the vibration characteristics, some doubt must arise as to the best value for any of these constants. For example, a set of possible constants given by Harp and Rasmussen (*ibid.*, p. 778), in which $K_{C=O}$ is $13{\cdot}43 \times 10^5$ dynes cm.$^{-1}$, when used to calculate the frequencies of the $A_1$ vibrations by the method used by Halverson and Williams gave the results shown below, in which the agreement with the observed values is

| | Frequencies: * | | | | Frequencies: * | | |
|---|---|---|---|---|---|---|---|
| Vibration | Calc. (1) | Calc. (2) | Obs. | Vibration | Calc. (1) | Calc. (2) | Obs. |
| CH | 3045 | 3046 | 3066 | C=C | 1086 | 1037 | 1120 |
| C=O | 2133 | 2168 | 2153 | $CH_2$ | 1409 | 1354 | 1386 |

* (1) By using $K_{C=O} = 15{\cdot}5$, $K_{C=O} = 9{\cdot}8$, $K_{CH} = 5{\cdot}23$, $k = 1{\cdot}5$ ($\times 10^5$ dynes cm.$^{-1}$), $K_{\delta CH_2}$ $0{\cdot}494 \times 10^{-11}$ erg/radian$^2$.
(2) By using $K_{C=O} = 13{\cdot}43$, $K_{C=O}$ 9·7, $K_{CH} = 5{\cdot}23$, $k = -0{\cdot}12$ ($\times 10^5$ dynes cm.$^{-1}$), $K_{\delta CH_2} =$ $0{\cdot}494 \times 10^{-11}$ erg/radian$^2$.

almost as good as that obtained when Halverson and Williams's force constants were used. It seems reasonably certain nevertheless that the carbonyl bond in keten has very similar characteristics to those of carbon dioxide and carbonyl sulphide.

There is obtained in this way considerable support for the belief that nickel tetracarbonyl with C–O bond distance 1·15 Å (Crawford and Horawitz, *J. Chem. Phys.*, 1948, **16**, 147) and bond-stretching force constant $15{\cdot}89 \times 10^5$ dyne cm.$^{-1}$ (Crawford and Cross, *ibid.*, 1938, **6**, 525) is best formulated as (II) in which the nickel atom forms double

bonds with the four carbon atoms (cf. Coulson, *op. cit.*, p. 216). One of the difficulties associated with the acceptance of structure (I) is the fact that it requires a relatively high negative formal charge on nickel which is improbable for a metal (cf. Pauling, Victor Henri Memorial Volume, Liége, 1948, p. 4; *J.*, 1948, 1461). The second structure minimises such formal charge effects and, except for ionic character produced by the difference in electronegativity of the bonded atoms, leaves the nickel neutral. An extension of this work to other carbonyls should yield valuable results, iron pentacarbonyl being now under investigation. In the sequence $Ni(CO)_4 \longrightarrow Fe(CO)_5 \longrightarrow Cr(CO)_6$ the bond-length data * have been interpreted to mean that double-bond character is steadily decreasing. At first sight this is to be expected because (*a*) the number of 3*d* electrons available for π-bond formation is decreasing along the above sequence (10 ⟶ 8 ⟶ 6); and (*b*) the total number of bonds required is increasing (4 ⟶ 5 ⟶ 6). Unfortunately, the problem is complicated by the fact that the σ-bond hybridisation is also changing along the series ($sp^3 \longrightarrow dsp^3 \longrightarrow d^2sp^3$) and this should affect both force-constant and bond-length data.

If two of the carbonyl groups are replaced by the chelate group, *o*-phenylenebisdimethylarsine (III) = diarsine, to form *o*-phenylenebisdimethylarsinedicarbonylnickel$^0$ (IV) (Nyholm, *J.*, 1952, 2906), the carbonyl bond-stretching frequencies are found to be 1940 and 1996 cm.$^{-1}$ (for solution in tetrachloroethylene). The splitting of the carbonyl absorption into two bands is similar to that observed in nickel tetracarbonyl itself which gives rise to bands at 2043 and 2050 cm.$^{-1}$. Although it is not possible to carry out a complete analysis of the spectrum and so calculate an accurate value for the C–O bond-stretching force constant, an approximate value can be obtained on the assumption that the 1940 and 1996 cm.$^{-1}$ absorption bands arise from vibrations confined to the carbonyl groups. A correction can be applied for interaction with the Ni–C vibration, for which Crawford and Cross (*loc. cit.*) give the frequency of about 348 cm.$^{-1}$. The value calculated in this way for the C–O bond-stretching force constant ($15{\cdot}0 \times 10^5$ dynes cm.$^{-1}$) may still be a little higher than the true value but the error is probably less than $\pm 0{\cdot}3 \times 10^5$ dynes cm.$^{-1}$.

## Experimental and Calculation

The spectrum of (IV) was measured with a Perkin Elmer Model 12C Spectrometer, a sodium chloride prism being used. The C–O bond-stretching force constant ($k$) was calculated by means of the formula

$$k = 4\pi^2 c^2 \nu^2 \mu_{CO} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $c$ = velocity of light, $\mu_{CO}$ = reduced mass of carbon and oxygen atoms, and $\nu$ = C–O bond stretching frquency, which is given by $\nu^2 = \frac{1}{2}(1940^2 + 1996^2)$. The effect of coupling of the C–O and Ni–C bond-stretching vibrations was estimated by using Matthieu's formula ("Spectres de Vibration et Symmetrie," Herman, Paris, 1947, p. 427), *viz.*,

$$\nu^2 = \nu^2_{CO}\left[1 + \frac{\alpha\nu^2_{Ni-C}}{\nu^2_{CO} - \nu^2_{Ni-C}}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where, $\nu_{CO}$ and $\nu_{Ni-C}$ are the bond-stretching frequencies without coupling of the vibrations, $\nu$ = observed carbonyl bond-stretching frequency (showing effect of coupling with the Ni–C vibration), and $\alpha$ = coupling coefficient given by

$$\alpha = \mu_{CO} \times \mu_{NiC}/m^2_C$$

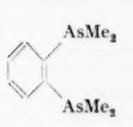
where $\mu_{CO}$ and $\mu_{NiC}$ are the reduced masses for the atoms concerned in the several vibrations and $m_C$ = mass of the carbon atom. From (1), $k = 15{\cdot}7 \times 10^5$ dynes cm.$^{-1}$. Application of (2) gives $\nu_{CO} = 1928$ cm.$^{-1}$ if $\nu_{NiC} = 500$ cm.$^{-1}$. This high value of the Ni–C bond stretching frequency was chosen to give an estimate of the upper limit of the effect of interaction on the carbonyl frequency. Use of $\nu_{CO} = 1928$ cm.$^{-1}$ in formula (1) gives $k = 15{\cdot}0 \times 10^5$ dynes cm.$^{-1}$.

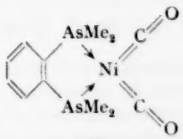
## Discussion

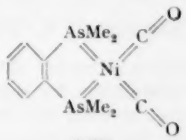
It is seen that replacement of two carbonyl groups by *o*-phenylenebisdimethylarsine to form the complex (IV) has had little effect on the character of the remaining two carb-

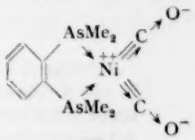
* The authors thank a Referee for raising this point.

onyl bonds, which are very similar to those of nickel tetracarbonyl. Two possibilities arise for the basic structure of the diarsine (IV), *viz.*, (IV*a*), in which the arsenic forms co-ordinate bonds with the nickel, and (IV*b*), in which nickel and arsenic are doubly bonded. An important difference between these structures lies in the fact that, whereas in (IV*b*) the


(III)


(IV*a*)

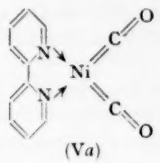

(IV*b*)

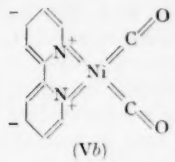

(IV*c*)

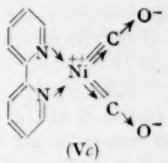
nickel atom is effectively neutral, yet in (IV*a*) it carries a negative formal charge. This could be dissipated through resonance with structures such as (IV*c*) which would have a considerable effect on the force constant of the carbonyl bond. It is concluded therefore that the most important structure for the diarsine complex is (IV*b*), in which the nickel forms double bonds with the arsenic.

It is significant in this connection that only those ligands which are capable of double-bond formation (*e.g.*, tertiary arsines and phosphines, *iso*cyanides) have been observed to replace the carbonyl groups of nickel tetracarbonyl, and that no compounds have been reported of ligands for which it is not possible to write feasible double-bond structures.

A similar investigation of the red dipyridyl complex (V) was attempted. Unfortunately, this compound is insoluble in solvents suitable for infra-red studies and had to be examined as a suspension in paraffin. Under these conditions the carbonyl frequencies were found to be 1861 and 1950 cm.$^{-1}$. Under similar conditions the frequencies for the diarsine were 1916 and 1977 cm.$^{-1}$, instead of 1940 and 1996 cm.$^{-1}$ when measured in dilute solution. If the frequencies of the dipyridyl complex are adjusted to allow for the effect of state as


(V*a*)


(V*b*)


(V*c*)

observed in the diarsine, and calculations are carried out as above, a C–O bond-stretching force constant of 14·4 × 10$^5$ dynes cm.$^{-1}$ is obtained. This suggests that the bond order is a little lower than in the diarsine, as might be expected if structure (V*c*) contributed to the resonance hybrid. This might be expected to play a more important part than in the diarsine since Ni–N double bond formation necessitates a separation of charge in the ligand. This necessity for charge separation would certainly mean that a full double bond between the nitrogen and the nickel as in (V*b*) is improbable, and this structure would only make a partial contribution to the resonance hybrid; this should be contrasted with the arsine bond where a complete double bond is feasible. This conclusion that dipyridyl has a smaller capacity for double-bond formation than diarsine lends some support for the conclusions derived from magnetic measurements (Burstall and Nyholm, *J.*, 1952, 3570).

The foregoing is considered to provide strong evidence for the postulate that in the above substituted nickel carbonyl complexes there is double-bond character in the Ni–As and Ni–N bonds. This conclusion supports the idea that double-bond character is possible in other metal–ligand bonds, as has frequently been suggested.

The authors acknowledge a gift of the nickel carbonyl used in this investigation from the Mond Nickel Co. They are also grateful to Professor D. P. Craig for helpful discussions on this paper.

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## 546. *Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part I. Edge-displacement as a Hypothesis linking Mechanism with Stereochemistry of Substitution.*

By D. D. Brown, C. K. Ingold, and R. S. Nyholm.

Owing to the differing geometry of the octahedron and tetrahedron, there is not a one-to-one correlation for substitution in octahedral molecules, as there is for tetrahedral, between the steric course of an individual molecular act of substitution and the steric course of substitution considered as defining the observable stereochemical relation between product and factor. The degree of correlation between the molecular and observable (microchemical and macrochemical) steric course of substitutions in octahedral molecules is defined, as a first step in setting up the problem of elucidating the circumstances which control the steric course in either sense of octahedral substitutions.

Analogy with carbon chemistry suggests that this problem is unlikely to be soluble without prior elucidation of the main mechanisms available for octahedral substitution, and the establishment of criteria for recognising them. A survey of the literature of octahedral substitutions suggests that some sort of duplexity of mechanism, which might well be a coexistence of the bimolecular and unimolecular mechanisms of nucleophilic substitution, is general.

### (1) *The Stereochemical Problem.*

(1*a*) *Types of Observed Stereo-change.*—Werner, more than 40 years ago, investigated the stereochemistry of substitutions at a six-co-ordinated atom. He showed that some substitutions involved *cis-trans*-changes while others preserved a *cis-* or *trans*-configuration. Ever since then, the problem has awaited solution, as to what controls the steric course of substitutions at octahedrally co-ordinated centres.

Werner dealt largely with nucleophilic substitutions, which introduced a group Y in place of a ligand X in the complex of a sexacovalent atom M, for instance, cobalt, having four similar non-replaced ligands R, such as four ammonia or two ethylenediamine molecules, as well as a non-replaced ligand A:

$$Y^- + MR_4AX \longrightarrow MR_4AY + X^- \quad . \ . \ . \ . \ . \ . \ . \ . \quad (S_N)$$

In the series of bisethylenediaminecobalt(III) complexes, he obtained every possible kind of stereochemical result, as the following examples illustrate (*Annalen*, 1912, **386**, 1):

$$\textit{cis}\text{-}[Co\ en_2(NH_3)Br]^{++} \xrightarrow{NH_3} \textit{cis}\text{-}[Co\ en_2(NH_3)_2]^{+++}$$

$$\textit{cis}\text{-}[Co\ en_2Cl(NH_3)]^{++} \xrightarrow{SCN^-} \textit{trans}\text{-}[Co\ en_2Cl(NCS)]^{+}$$

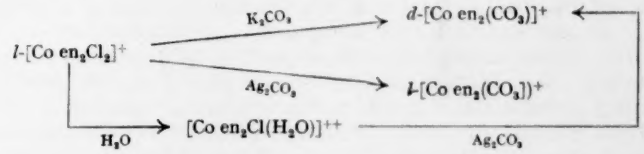
$$\textit{trans}\text{-}[Co\ en_2Cl(NH_3)]^{++} \xrightarrow{NO_2^-} \textit{trans}\text{-}[Co\ en_2Cl(NO_2)]^{+}$$

$$\textit{trans}\text{-}[Co\ en_2(NH_3)Cl]^{++} \xrightarrow{OH^-} \textit{cis}\text{-}[Co\ en_2(NH_3)(OH)]^{++}$$

Bailar and his co-workers have emphasized another espect of the matter. By treating the *l-cis*-dichlorobisethylenediaminecobalt(III) ion in aqueous solution with excess of silver carbonate, they could obtain the *l*-carbonatobisethylenediaminecobalt(III) ion (Bailar and Auten, *J. Amer. Chem. Soc.*, 1934, **56**, 774; Bailar, Jonelis, and Hoffman, *ibid.*, 1936, **58**, 2224), although, as Werner and McCutcheon had shown previously, the action of potassium carbonate in water produced the *d*-carbonato-ion * (*Ber.*, 1912, **45**,

* For purposes of identification, Werner's prefixes, *d* and *l*, are employed, essentially as historical dockets. There are difficulties in labelling by sign of rotation, (+) and (−), since sign often depends on wave-length. Thus the above *l*-dichloro-ion is (−) to cadmium red, but (+) to sodium yellow light. The subject is not advanced enough to justify an attempt to employ configurational symbols, such as *D* and *L*, for the labelling of specific substances.

3281). On keeping the aqueous solution of the *l*-dichloro-ion before adding the silver carbonate, the *d*-carbonato-ion was obtained (Bailar and Peppard, *J. Amer. Chem. Soc.*, 1940, **62**, 820). This altered result is due to the intervention of an additional stage of substitution, namely, monoaquation of the dichloro-ion, as is made clear by comparison of the known rate of this process (Mathieu, *Bull. Soc. chim.*, 1936, **3**, 2121, 2151) with the variations of rotation of the formed carbonato-ion with time of previous keeping of the dichloro-solution :




The *l*-dichloro-ion was also converted into the *cis*-diammino-ion with either the *d*- or the *l*-form in excess, by treatment with liquid ammonia at suitably regulated temperatures (Bailar, Haslam, and Jones, *J. Amer. Chem. Soc.*, 1936, **58**, 2226) :

$$l\text{-}[Co\ en_2Cl_2]^+ \xrightarrow{NH_3} \text{either } d\text{- or } l\text{-}[Co\ en_2(NH_3)_2]^{+++}$$

These conversion schemes obviously involve changes of configuration, though we cannot with certainty locate the latter.

(1*b*) *Edge-displacement as a Unifying Hypothesis.*—Bailar and his co-workers have claimed the described changes as the first Walden inversions of inorganic chemistry; but the implied correspondence to inversion in organic chemistry is misleading. Not only does it suggest a geometrical inversion of the covalencies, a more radical reorganisation than need be assumed, but also it implies a deeper distinction than can justifiably be drawn between *d*–*l*-conversions and *cis*–*trans*-changes in octahedral substitutions. These *d*–*l*- and *cis*–*trans*-changes are not as different as are some similarly described changes of carbon compounds : either type of change can arise in the octahedral system as a result of what we may call *edge-displacement*, which can be represented thus :

How we observe, and how we describe this change depends, not on the groups Y, R, and X directly concerned, but on the position of some unaffected group A, whose relation to the replaced and replacing groups X and Y is being denoted by the prefixes *d* and *l*, or *cis* and *trans*. If A is at (1), we shall describe the above process as *cis* ⟶ *trans*, if at (2), as *trans* ⟶ *cis*, and if at (3) or (4), as either *d* ⟶ *l* or *l* ⟶ *d*. But the substitution is of just the same stereochemical nature in all cases.

We may, then, look upon changes either of optical or of geometrical configuration as manifestations of a single stereochemical mode of substitution, that of edge-displacement. However, it is to be noticed that, although any observed stereo-change can be understood as an edge-displacement, an observed absence of a stereo-change in octahedral substitution does not always imply the absence of an edge-displacement. If, in the preceding diagram, the groups in positions (1) and (2), and likewise those in positions (3) and (4), can be superposed either on the other by a rotation of the molecule, then in the represented substitution with edge-displacement, a *cis*-factor will give a *cis*-product, chemically identical with that which would be given by substitution without edge-displacement. If the above geometrical condition is satisfied, together with the further condition that the groups in positions (3) and (4) cannot be superposed either on the other by reflexion, then the substitution with edge-displacement will convert a *D-cis*-factor into a *D-cis*-product, or an *L-cis*-factor into

an *L-cis*-product, optically, as well as chemically, identical with the product which would be formed in substitution without edge-displacement.* Such is the case, for instance, when the positions (1) and (3) and the positions (2) and (4) are identically coupled, as by ethylenediamine molecules. Thus the experimental fact, that substitution sometimes occurs without stereo-change, does not lead, without further consideration, to the conclusion that substitution can occur without edge-displacement.

However, a *trans*-compound, $MR_4AX$, on substitution with edge-displacement must yield a *cis*-product $MR_4AY$; for one of the R's will take the place of X, while Y will take the place of the R, and all four R's were originally *cis*- with respect to A. Therefore an observation that a *trans*-factor yields a *trans*-product does imply substitution without edge-displacement. Now Werner observed several *trans* ⟶ *trans* substitutions; and therefore we may provisionally conclude † that octahedral substitution can occur both with and without edge-displacement. Thus we should expect stereochemical laws for octahedral substitutions at least as complicated as those of tetrahedral substitutions, which in carbon chemistry may occur both with and without inversion.

From the above discussion it will be clear that the fields of incidence of stereo-change and of edge-displacement are not co-extensive. The relation between them for the structures of concern to us here is schematically shown in Table 1. The importance of appreciating the difference between the ranges of incursion of observable stereo-change and of edge-displacement is that the latter, referring, as it does, to a process, rather than immediately to the product, is likely to be the more intimately related to substitution mechanism, and therefore to be subject to simpler stereochemical laws dependent on mechanism, than any which could be framed for direct application to observed stereo-change.

TABLE 1. *Relation of stereo-change to edge-displacement in nucleophilic substitutions in octahedral complexes* $MR_4AX$.

<table>
<tr><td colspan="5"></td><td colspan="3">Substitution without edge-displacement</td></tr>
<tr><td colspan="2">Stereo-change</td><td colspan="3">No stereo-change</td></tr>
<tr><td>cis ⟷ trans</td><td>D ⟷ L</td><td>D ⟷ D<br>L ⟷ L</td><td>cis ⟷ cis</td><td>trans ⟷ trans</td></tr>
<tr><td colspan="3">Substitution with edge-displacement</td><td colspan="3"></td></tr>
</table>

Werner having established changes of configuration during octahedral substitutions, it seems curious that so many configurations should have been assigned on the assumption that no stereo-changes are involved in the conversions which form the basis of the assignment. Werner himself slipped slightly from rigour in that, in several cases in which a genetic chain admits more than one stereochemical interpretation, he adopts the one with the smallest number of stereo-changes, as though there were some natural law of economy in such changes. However, the blind eye has been turned on possible stereo-changes so much since, that an appreciable proportion of present assignments of configuration cannot be trusted. We known that Erdmann's salt, $NH_4^+[Co(NH_3)_2(NO_2)_4]^-$, was regarded as a *cis*-diammine, because by substitution it gave an optically resolvable and therefore *cis*-diammino-oxalato-salt, $NH_4^+[Co(NH_3)_2(NO_2)_2(C_2O_4)]^-$, until Wells showed by *X*-ray analysis that the original substance is a *trans*-diammine (*Z. Krist.*, 1936, **95**, 74). We have taken the view that, for our purposes, configurations are certain which are based on any of the following criteria: (1) *X*-ray analyses, provided that we have spectral or other evidence that no change of stereo-form occurs between the crystal state and solution, (2) a distinction

* Capital-letter prefixes are here employed, since the reference is to configurational relationships.

† "Provisionally" because, in the absence of kinetic data, we have no proof that the *trans* ⟶ *trans* substitutions described by Werner go in one step, that is, without an intermediate solvolytic substitution, *i.e.*, aquation.

of optical resolvability, and (3) a genetic chain which does not involve the breaking of a ligand–metal bond.

(2) *The Problem of Substitution Mechanism.*

The stereochemical problem has now been set up in a form convenient for further treatment. But, as the history of the corresponding task of carbon chemistry suggests, the treatment is unlikely to make rapid headway, unless the problem of substitution mechanism is simultaneously solved. For if more than one mechanism operates, each will have its own spatial rules; and then, the unsifted stereochemical observations will give no answer: they must be separated according to mechanism. Therefore our next proceeding is to consider existing evidence for multiplicity of mechanism in octahedral substitutions.

(2*a*) *Indications of a Bimolecular Mechanism of Octahedral Substitution.*—The kinetics of octahedral substitutions have been studied by a number of authors, but the whole of the work has been done in solvent water, whose molecules have a higher nucleophilic (complexing) power towards the ions of transition metals than have the molecules of any other common solvent, except liquid ammonia. It may be on this account that the only substituting agent, controlled with respect to concentration as a solute, for which a definite kinetic order has been firmly established, is the strongly nucleophilic hydroxide ion. It has been shown that the replacement of halogen in the bromo- or chloro-pentamminocobalt(III) ion by hydroxyl, through reaction with alkali hydroxide, is kinetically of the second order (Brönsted and Livingstone, *J. Amer. Chem. Soc.*, 1927, **49**, 435; Puente, *Anal. Asoc. Quim. Argentina*, 1943, **31**, 5),* and therefore we have some grounds for a tentative inference that these are $S_N2$ reactions, that is, bimolecular nucleophilic substitutions (like the alkaline hydrolysis of methyl chloride):

$$OH^- + [Co(NH_3)_5X]^{++} \longrightarrow [Co(NH_3)_5(OH)]^{++} + X^- \quad . \ . \ . \ . \quad (S_N2)$$

The kinetic evidence is, however, not quite unequivocal, because the same kinetics are required by two other mechanisms, labelled $S_N1cB$ and $S_N2cB$, that is, unimolecular substitution in the conjugate base of the cobaltammine (as in the alkaline hydrolysis of chloroform), and bimolecular substitution in the conjugate base (some probable examples of such substitution are mentioned below). In the present application of these mechanisms a proton would first be removed from one of the ammonia ligands by the reagent hydroxide ion, and then the conjugate base so produced would lose a halide ion, with the subsequent or simultaneous uptake of the ions of water. Ways are known by which the straightforward mechanism $S_N2$ can be distinguished from these conjugate-base mechanisms; but they have not yet been applied to the cases discussed.

The reaction which is usually dominating in aqueous solution, even in the presence of some anions, is solvolytic aquation, the kinetics of which have been followed for replacement by water of chloro-, bromo-, and nitrato-groups from the pentamminocobalt(III) ions (Lamb and Marden, *J. Amer. Chem. Soc.*, 1911, **33**, 1873; Brönsted, *Z. physikal. Chem.*, 1926, **122**, 386; Garrick, *Trans. Faraday Soc.*, 1937, **33**, 486; Adell, *Z. anorg. Chem.*, 1941, **246**, 303), of chloro-, bromo-, iodo-, and nitrato-groups from the pentamminoiridium(III) ions (Lamb and Fairhall, *J. Amer. Chem. Soc.*, 1923, **45**, 378), and of chloro-, bromo-, and iodo-groups from the pentamminochromium(III) ions (Freundlich and Bartels, *Z. physikal. Chem.*, 1922, **101**, 177):

$$H_2O + [M(NH_3)_5X]^{++} \longrightarrow [M(NH_3)_5(H_2O)]^{+++} + X^-$$

These are first-order reactions, but this result does not disclose mechanism. Some support may, however, be adduced for the view that the substitutions in the cobalt complexes are bimolecular, with a water molecule as the second reactant; for the rates of displacement of chloro-, bromo-, and nitrato-groups from these complexes are nearly in the same ratios

* Observed second-order kinetics in the replacement of an acetato- or substituted acetato-group in the appropriate acetatopentamminocobalt(III) ion by a hydroxyl group in reaction with aqueous alkali (Basolo, Bergmann, and Pearson, *J. Phys. Chem.*, 1952, **56**, 22) cannot be accepted as evidence of the kinetics of substitution at cobalt in the absence of a demonstration that the metal–oxygen bond, rather than the acyl–oxygen bond, is broken in this substitution; for the carboxyl mechanism $B_{Ac}2$ might here be under observation (cf. Bunton and Llewellyn, forthcoming paper).

for the first-order reactions with solvent water as for the second-order reactions with hydroxide ions. It seems unlikely that the agreement, shown in Table 2, would be so close if the mechanisms differed fundamentally, and the most obvious interpretation is that all these substitutions take place by mechanism $S_N2$.

TABLE 2. *Rates of displacement of* X *from* $[Co(NH_3)_5X]^{++}$ *by water and by hydroxide ions.*

| | Rates | | | Ratios | |
|---|---|---|---|---|---|
| X displaced | Cl | Br | $NO_3$ | Cl/Br | $Br/NO_3$ |
| By $H_2O$ { $10^5k_1$, 25°, $k_1$ in sec.$^{-1}$ | 0·16 | 0·65 | 3·00 | 4·1 | 4·6 |
| By $H_2O$ { „ 15°, „ | — | 0·16 | 0·60 | — | 3·8 |
| By $OH^-$ { $k_2$ in sec.$^{-1}$ mole$^{-1}$ l., 25° | 1·30 | 5·93 | — | 4·6 | — |
| By $OH^-$ { „ „ 15° | — | 1·42 | 5·91 | — | 4·1 |

Measurements of the rate of solvolytic displacement by water of chloro- and nitrato-groups from the relevant aquotetrammino- or aquobisethylenediamine-cobalt(III) ions have shown that the substitution goes partly through the conjugate base of the original aquo-compound, as illustrated below, to an extent depending in the expected manner on the pH (Brönsted, *Z. physikal. Chem.*, 1926, **122**, 383; Matsuno, *Bull. Chem. Soc. Japan*, 1926, **1**, 133; Tsuchida, *ibid.*, 1936, **11**, 721; Brüll, *Compt. rend.*, 1936, **202**, 1584; 1937, **204**, 349; Mathieu, *Bull. Soc. chim.*, 1936, **3**, 2121, 2152; 1937, **4**, 687; Ovenston, Thesis, London, 1936):

$$\begin{array}{ccc} [Co\ en_2(H_2O)Cl]^{++} & \xrightarrow{S_N2} & [Co\ en_2(H_2O)_2]^{+++} \\ \downarrow & & \uparrow \\ [Co\ en_2(OH)Cl]^{+} & \xrightarrow{S_N2cB} & [Co\ en_2(OH)(H_2O)]^{++} \end{array}$$

There is, however, no indication in these results of a fundamental difference of mechanism of substitution, which we suppose to be bimolecular, that is, $S_N2$ or $S_N2cB$ as indicated. It is implied that there is no difference in the type of binding of the displaceable ligand in the presence of the aquo-groups.*

(2*b*) *Indications of a Unimolecular Mechanism in Octahedral Substitution.*—That bond type may not be generally retained in the presence of aquo-groups is indicated by observations on the isotopic exchange of ligands and of central metal ions. Ligand exchanges occur at widely different rates in water: the exchange of chloride ion with chlorine in $[Co\ en_2Cl_2]^+$ takes place too slowly to compete with aquation (Ettle and Johnson, *J.*, 1939, 1490), while that of bromide ion with bromine in $[PtBr_6]^{--}$ occurs too rapidly for measurement (Grinberg, *Bull. Acad. Sci. U.S.S.R.*, 1940, **4**, 342). The chromic ion has been shown, by the use of $H_2{}^{18}O$ to exist in water as $[Cr(H_2O)_6]^{+++}$, evidently a covalently bonded complex, since it exchanges its water ligands only slowly. Theory teaches that these covalencies are constructed from $d^2sp^3$ chromium orbitals. On the other hand, the hydrated ferric ion, $[Fe(H_2O)_6]^{+++}$, whose magnetic moment shows that it is not using the orbitals needed to hold the water by similarly constituted bonds, exchanges the water very rapidly (Hunt and Taube, *J. Chem. Phys.*, 1951, **19**, 602). The present approach to the description of such labile bonds is to regard them as formed from $sp^3d^2$ orbitals, that is, as involving higher *d* orbitals (4*d* in the example cited), which, by carrying the bonding electrons far from the central nucleus, produce bonds both highly polar and very easily heterolysed (Taube, *Chem. Reviews*, 1952, **50**, 69; Burstall and Nyholm, *J.*, 1952, 3570; Nyholm and Sharpe, *ibid.*, p. 3579; Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, in the press). The ions $[Ni(CN)_4]^{--}$ and $[Pd(CN)_4]^{--}$ exchange ligands with labelled cyanide ion too rapidly for measurement, but the ions $[Cr(CN)_6]^{---}$, $[Co(CN)_6]^{---}$, $[Fe(CN)_6]^{---}$, and $[Fe(CN)_6]^{----}$ do so too slowly, while the ion $[Mn(CN)_6]^{---}$ undergoes the exchange at a measurable rate, which, significantly, is of zero order with respect to cyanide ion (Adam-

* Unimolecular aquation of cobalt complexes has been suggested by Pearson, Boston, and Basolo (*J. Amer. Chem. Soc.*, 1952, **74**, 2944), but only on the basis of a much over-simplified discussion of structural effects on reaction rate, a discussion which, in particular, takes no account of polar effects.

son, Welker, and Volpe, *J. Amer. Chem. Soc.*, 1950, **72**, 4030; Adamson, Welker, and Wright, *ibid.*, 1951, **73**, 4786).

In a number of cases, rates of metal-ion exchange appear qualitatively at least to follow those of ligand exchange. Metal exchanges of $[Ni\ en_3]^{++}$, and some other forms of nickel(II), with $[Ni(CN)_4]^{--}$ are rapid (Long, *J. Amer. Chem. Soc.*, 1951, **73**, 537), but that of $[Cr(H_2O)_6]^{+++}$ with $[Cr(CN)_6]^{---}$ is very slow (Menker and Garner, *ibid.*, 1949, **71**, 371), as is that of $[Co(H_2O)_6]^{+++}$ with $[Co(NH_3)_6]^{+++}$ and with $[Co(CN)_6]^{---}$ (Hoshowsky, Holmes, and McCallum, *Canadian J. Res.*, 1949, **27**, *B*, 258). Exchange between aqueous $Ni^{++}$ and $[Ni\ dipy_3]^{++}$, where " dipy " stands for 2 : 2′-dipyridyl, is stated to be nearly complete in 90 min. at room temperature (Johnson and Hall, *J. Amer. Chem. Soc.*, 1948, **70**, 2344), while the optically active dipyridyl complex is reported to racemise in water with a half-life of 15 min. at 17° (Morgan and Burstall, *J.*, 1931, 2213). Exchange of aqueous $Fe^{++}$ with $[Fe\ dipy_3]^{++}$ proceeds to the extent of about 25% in 120 min. at room temperature (Ruben, Kamen, Allen, and Nahinsky, *J. Amer. Chem. Soc.*, 1942, **64**, 2297), whereas the half-life for racemisation of the optically active complex in water is recorded as 75 min. at 17·5° (N. R. Davies and F. P. Dwyer, personal communication). The exchange of aqueous $Fe^{++}$ with $[Fe\ ophen_3]^{++}$, where " ophen " represents *o*-phenanthroline, has a half-life of 100 min. at room temperature (Ruben *et al.*, *loc. cit.*), while the optically active phenanthroline complex racemises with a half-life of 121 min. at 15° (Davies and Dwyer, personal communication).

The concept of the exchange of central metal ions in a single bimolecular stage is very difficult. The picture which the foregoing observations suggest as applying to certain cases, though probably not in this simple form to all, is that of rate control by a reaction rupturing the first metal–ligand bond, all subsequent stages of breakdown and resynthesis being more rapid. We could then understand why rates of ligand exchange and metal exchange seem often to follow each other, and why a number of rates of racemisation and of exchange of the central metal are of the same order of magnitude. If in aqueous solution the rate-controlling first step involved either a mono-aquation, or the simple heterolysis of one ligand, we could understand how a rate of cyanide exchange could be independent of the concentration of cyanide ions.

Now it is probable that, for some central ions at least, aquation can so change bond-type as to lead to ready heterolysis. We know from magnetic data, as well as from chemical considerations, that $[Fe(CN)_6]^{---}$ has strong, essentially covalent bonds, formed, it is presumed, with the aid of $d^2sp^3$ iron orbitals, whereas $[Fe(H_2O)_6]^{+++}$, which does not contain such bonds, is a structure of covalent, highly polar and therefore very easily heterolysed bonds, formed, as it is believed, with upper-$d$-containing $sp^3d^2$ orbitals. Therefore, the sequence of substitutions which would convert the former complex ion into the latter, although it doubtless starts with some stages of bimolecular aquation, as would assist displacement of the originally strongly bound ligands, is likely, as the binding becomes more labile and more polar, to end with substitutions resulting from spontaneous heterolysis, that is, with stages of unimolecular aquation. We expect the main changes of bond type to occur together in all the bonds of the central metal, even when two kinds of ligands are being bound, because bond constitutions are linked by orbital occupancy in the central atom, and thus with the numbers of unpaired spins. Moreover, the major changes of bond constitution are likely to occur at some one stage of the series of stages of substitution, because the sharply alternative modes of spin coupling will resist slow gradations. Thus we can reasonably look for a somewhat sudden change, at some stage, from a bimolecular to a unimolecular mode of displacement of the ligands. If our series of substitutions, instead of consisting in the conversion of $[Fe(CN)_6]^{---}$ into $[Fe(H_2O)_6]^{+++}$, had consisted in the conversion of $[Fe\ ophen_3]^{++}$ into $[Fe(H_2O)_6]^{++}$, then the near-equivalence of the iron exchange rate and the racemisation rate would give reason for thinking that the change of mechanism probably occurs between the first stage of substitution and the second.

What has been said of aqueous iron(II) and iron(III) complexes is probably equally true of nickel(II) complexes, but not of cobalt(III) and chromium(III) complexes. Optically active mono- and di-aquocobalt(III) complexes, *e.g.*, $[Co\ en_2(NO_2)(H_2O)]^{++}$, $[Co\ en_2Cl(H_2O)]^{++}$, and $[Co\ en_2(H_2O)_2]^{+++}$, have been prepared (Werner, *Ber.*, 1911, **44**,

3272; Mathieu, *Bull. Soc. chim.*, 1937, **4**, 687). There is magnetic evidence that $[Co(H_2O)_6]^{+++}$, and isotopic evidence that $[Cr(H_2O)_6]^{+++}$ have strong covalencies. Consistently, cobalt(III) and chromium(III) are among the central metal ions which have not been observed to undergo metal-ion exchange. Thus the stages of successive aquation of complex ions of cobalt and chromium might remain bimolecular to the end (at least, the constitutions of the products do not prove otherwise), whereas those of the complex ions of iron and nickel should go into the unimolecular form as heterolysis of the ligands becomes easier. However, if we should work in a solvent of much smaller complexing power than water, then a switch from the bimolecular to the unimolecular mechanism might occur in the early stages of solvolysis even of cobalt and chromium complexes; and when heterolysis of the ligands occurs sufficiently readily, then non-solvolytic substitutions, as by weakly nucleophilic anions, could be unimolecular. In planning work based on Werner's, it is natural to think first of the aqueous reactions of cobalt ions; but whether we then widen the field by including other metals, or by going over to other solvents, the above survey suggests that we must expect to encounter both the bimolecular and the unimolecular mechanisms of substitution—$S_N2$ and $S_N1$—and perhaps intermediate, or even quite different mechanisms also.

Actually we have commenced our experimental study by using cobalt complexes. However, we have employed as solvent, not only water, as when strongly nucleophilic reagents were under examination, but also, and extensively, the very much more feebly complexing solvent, methyl alcohol, the purpose being to repress solvolytic substitution when a weakly nucleophilic solute was the intended reagent. Within this range of experience, we do indeed find both the standard mechanisms of substitution; and our survey suggests that we should accept this finding as typical for octahedral substitutions in general.

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## 547. *Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part II.* Kinetics and Molecularity of Nucleophilic Substitutions in the* cis-*Dichlorobisethylenediaminecobalt*(III) *Ion.*

By D. D. Brown and C. K. Ingold.

The kinetics of substitutions by 7 anions which displace chlorine from the *cis*-dichlorobisethylenediaminecobalt(III) ion have been studied in solvent methyl alcohol by polarimetric, spectroscopic, chemical, and radiochemical methods, as far as was in each case appropriate and convenient. For 4 of the anionic reagents, all weakly nucleophilic, substitution has $S_N1$ kinetics, and a common absolute rate, which is also the rate at which the original cation loses optical activity in the absence of stronger nucleophilic substituting agents. The expected ionic-strength and mass-law effects have been observed. For 3 anions, all more strongly nucleophilic, substitution has $S_N2$ kinetics, with rates differing widely, in order of nucleophilic power. The rate relations indicate that the nucleophilic attack is on the metal atom. These results closely parallel what was demonstrated by Gleave, Hughes, and Ingold in 1935 for nucleophilic substitution on carbon, and are considered to justify an extension of the concept of dual mechanism to substitution on cobalt, and tentatively, in view of the arguments of Part I, to octahedral substitutions generally.

### (1) *Preliminary Survey.*

We describe here the kinetic course of a number of substitutions in which one chlorine atom is displaced as chloride ion from the *cis*-dichlorobisethylenediaminecobalt(III) ion by various anionic substituting agents, ranging in complexing power from the weakly

* Part I, preceding paper.

nucleophilic nitrate and chloride ions, through bromide, thiocyanate, and nitrite ions, to the successively more nucleophilic azide ion and methoxide ion, the solvent being methyl alcohol throughout :

$$cis\text{-}[Co\ en_2Cl_2]^+ + X^- \longrightarrow [Co\ en_2ClX]^+ + Cl^-$$
$$X^- = NO_3^-, Cl^-, Br^-, SCN^-, NO_2^-, N_3^-, OMe^-$$

We shall deal with the observed kinetic orders, and the absolute and relative rates of the substitutions; and also with the conclusions which can be drawn concerning their molecularity. The results will establish duplexity of mechanism in this range of substitutions. In other papers we shall consider the steric course of some of the substitutions.

In order to be able to compare the rates of the substitutions it was necessary to employ the same solvent throughout. Water was unsuitable, since, owing to its high complexing power, it would have usurped the function of substituting agent at the weakly nucleophilic end of the anion series (Part I, Section 2). A solvent of low complexing power was required. There are many sueh solvents; but only a few of them are able to dissolve the salts which it was proposed to use in concentrations sufficient to permit the type of kinetic investigation planned. Methyl alcohol and ethylene glycol are among these few solvents, and methyl alcohol was selected as being generally the more convenient.

The choice of a *cis*- rather than a *trans*-form of halogeno-cobalt complex for this first experimental study of the mechanism of substitutions displacing halogen from cobalt complexes, followed from our decision to use an optically active complex. This plan arose in part from a desire to have the polarimetric method, in addition to other methods, available for following the kinetics of the substitutions. It also looked ahead to subsequent studies on the steric direction of substitutions; for a comparison of the rate of an isotopic substitution of halogen with the rate of concomitant loss of optical activity must evidently throw light on the stereochemistry of the substitution.

The selection of the particular *cis*-complex used in this work was determined by a preliminary survey of the optical rotatory and absorption spectra of a number of *cis*-cations. Salts of each of the *cis*-series, $[Co\ en_2Cl_2]^+X^-$, $[Co\ en_2(NCS)Cl]^+X^-$, $[Co\ en_2(NCS)Br]^+X^-$, $[Co\ en_2(NH_3)Cl]^{++}X_2^-$, and $[Co\ en_2(NH_3)Br]^{++}X_2^-$ were prepared and resolved by way of their (+)-α-bromocamphor-π-sulphonates. They were examined with respect to their rotation and absorption in methyl alcohol. Of the above cations, only the first gave rotations which, in the dilute solutions to be employed in the kinetic studies, were large enough to permit accurate kinetic observations at wave-lengths which were convenient for the light source and to the detecting eye, and were not too strongly absorbed by the solutions. We knew that the use of a dichloro-cation involved the consequence that displacement of the first chlorine atom might be kinetically overlapped by displacement of the second; we expected to be able to avoid this complication, where necessary, by studying initial rates of reaction.

For the unsymmetrical substitutions, that is, displacements of a chlorine atom from the dichloro-cation by reaction with any of the listed anions except chloride ion, we had available three kinetic methods, namely, the polarimetric method, the spectrophotometric method, and the method of chemical analysis, usually a matter of following the liberation of chloride ion by potentiometric titration. For the symmetrical substitution, that is, displacement of the bound chlorine by reaction with chloride ion, we used the radioisotope $^{36}Cl$, of half-life about $10^5$ years, for isotopic label; and thus we again had available three kinetic methods, namely, the polarimetric and spectrophotometric methods, and measurement of the transfer of radioactivity. But because of the special nature of this reaction, only the radioactivity method allows a direct deduction of the rate of substitution, though we have been able to find relations between this rate and the polarimetric and spectrophotometric rates. The polarimetric rate proved to be important for the present discussion of the molecularity of substitution. The spectrophotometric rate is relevant to the investigation of the spatial direction of substitution, as described in the next paper.

In the Sections 2—8, we consider results concerning the kinetics and molecularity of substitution, first for the symmetrical case of substitution by chloride ions, and then for unsymmetrical substitutions, notably by thiocyanate ion, for which the kinetic form of

reaction is similar, and by azide ion, for which it is different. These three examples mark out the pattern of the results, which we shall then fill in by reference to the reactions of the other anions already listed. In Section 9 (p. 2692) the results will be collectively discussed.

(2) *Action of Chloride Ion on the* cis-*Dichloro-cation.*

(2*a*) *Loss of Optical Activity from the Dichlorocobalt*(III) *Chloride.*—That enantiomer of the *cis*-dichlorobisethylenediaminecobalt(III) ion which gives the less water-soluble (+)-α-bromocamphor-π-sulphonate was designated by Werner as the *l*-form. Werner's label doubtless derives from the circumstance that he measured rotations using cadmium red light, for which the cation is lævorotatory. We retain Werner's label, although for our polarimetric kinetics we used sodium yellow light, for which the cation is strongly dextrorotatory. The rotation and absorption spectra of the cation in methyl alcohol are shown in Fig. 3 and 4 respectively (p. 2686). For sodium light we find $[M_D]$ +2520°. Mathieu reports $[M_D]$ +2000° (*Bull. Soc. chim.*, 1936, **3**, 463, 476), while Bailar, Haslam, and Jones give $[M_D]$ +1850° (*J. Amer. Chem. Soc.*, 1936, **58**, 2226) for aqueous solutions.

In solution in anhydrous methyl alcohol, the *l*-dichlorocobalt(III) chloride loses its optical activity gradually, but completely, according to a first-order law. This, then, is not a mutarotation, such as was found by Mathieu to accompany conversion of the di-

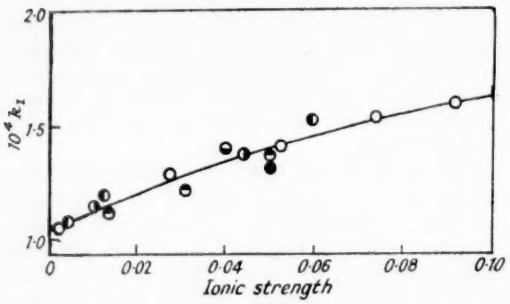



FIG. 1. *First-order rate constants for substitution in* cis-$[Co\ en_2Cl_2]^+$ *in* MeOH *at* 35·8°.

○ Substitution by $Cl^-$, polarimetric.
◒ ,, ,, ,, radioactivity.
◓ ,, ,, $NCS^-$, polarimetric.
● ,, ,, ,, spectrophotometric.
◐ ,, ,, $Br^-$, polarimetric.
◑ ,, ,, $NO_3^-$, polarimetric.

chloro-salt into the chloroaquo-salt in aqueous solution (*Bull. Soc. chim.*, 1937, **4**, 687). In methyl alcohol the optically inactive product still has the composition of the dichloro-salt. The rate law shows that no optically active intermediate of appreciable concentration intervenes between the active factor and inactive product. This isomeric conversion in methyl alcohol is about 9 times slower than the aquation studied by Mathieu in solvent water.

The first-order reaction in methyl alcohol is of zero order with respect to chloride ion. This was shown, in the first place, by adding excess of chloride ion in the form of lithium chloride. Even when a 50-fold excess was thus supplied, the first-order rate-constant, $k_1^{pol\text{-}Cl}$, was increased only by a factor of 1·5, as is shown in Table 1. A graph is given in

TABLE 1.—*Rate of loss of optical activity from* $[Co\ en_2Cl_2]^+Cl^-$ *alone and in the presence of* LiCl *in* MeOH *at* 35·8°.

| Run No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $[\{Co\ en_2Cl_2\}^+Cl^-]$ (mmole/l.) | 1·75 | 1·92 | 2·12 | 1·79 | 1·76 |
| [LiCl] (mmole/l.) | — | 25·2 | 50·0 | 72·0 | 90·2 |
| $10^3\mu$ ($\mu$ = ionic strength) | 1·75 | 27·1 | 52·1 | 73·8 | 92·0 |
| $[Cl^-]/[\{Co\ en_2Cl_2\}^+]$ | 1·0 | 14·1 | 24·6 | 41·2 | 52·3 |
| $10^4 k_1^{pol\text{-}Cl}$ (with $k_1$ in sec.$^{-1}$) | 1·05 | 1·28 | 1·40 | 1·52 | 1·58 |

Fig. 1, partly for comparison with rates obtained by other methods and reported below. Obviously this small rate-change is a salt effect. Account being taken of differences of solvent, it is of the same order of magnitude as some of the ionic-strength effects associated with the unimolecular substitutions of alkyl halides in hydroxylic solvents (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979).

The conclusion that the reaction rate is not specifically dependent on chloride ion would not be remarkable if the chloride ion did not stoicheiometrically intervene; but we shall show that it does. The kinetic conclusion itself will be amplified in later Sections, where we show that chloride ion can be replaced by other anions, which likewise act as substituting agents, but do so without affecting the rate of the loss of optical activity which accompanies their substitution.

The process leading to loss of optical activity from the dichlorocobalt(III) chloride in methyl alcohol is formally shown to be activated by measurement of the temperature coefficient of the reaction rate. The data in Table 2 give a good Arrhenius plot, leading to the value 22·64 kcal./mole for the activation energy, and $1{\cdot}07 \times 10^{12}$ sec.$^{-1}$ for the frequency factor.

TABLE 2. *Temperature dependence of the rate of loss of optical activity from* $[Co\ en_2Cl_2]^+Cl^-$ *in* MeOH.

| Run No. | 6 | 1 | 7 | 8 |
|---|---|---|---|---|
| $[\{Co\ en_2Cl_2\}^+Cl^-]$ (mmole/l.) | 1·77 | 1·75 | 2·06 | 1·92 |
| $T° - 273{\cdot}16°$ | 26·31 | 35·84 | 45·43 | 53·83 |
| $10^4 k_1^{pol\text{-}Cl}$ (with $k_1$ in sec.$^{-1}$) | 0·313 | 1·05 | 3·07 | 7·95 |

(*2b*) *Constancy of Chloride-ion Concentration during and after Rotation Loss.*—Chemical analysis can show whether or not chloride ion is liberated permanently or temporarily from the complex cation under the conditions of the rotation loss. It can also determine whether the product formed by rotation loss subsequently proceeds to liberate chloride ion.

Previous workers have reported difficulty in titrating chloride ion by silver ion in aqueous solutions of the dichlorocobalt(III) chloride. This is due in part to the rapidity of aquation (Mathieu, *Bull. Soc. chim.*, 1936, **3**, 2121, 2152). It is due in part also to a specific interaction between silver salts and the dichloro-cation (Werner, *Annalen*, 1912, **386**, 93). Mathieu obtained some success by potentiometric titration at 0°. In our experience, potentiometric titration in methyl alcohol at 0° works fairly well. We found that the end-points are sharpened if the methyl-alcoholic solution is diluted with 4 vols. of acetone. Table 3 records some estimations of chloride ion made at different times during the rotation loss, and also after it was substantially complete.

TABLE 3. *Estimated percentage of* $Cl^-$ *in cis-*$[Co\ en_2Cl_2]^+Cl^-$ *at various times after dissolution in* MeOH *at* 35·8°.

(Time of half-change for rotation loss = 1·8 hours.)

| Time (hours) | 0·25 | 0·75 | 4·5 | 13·0 |
|---|---|---|---|---|
| % $Cl^-$ (by titration in MeOH alone) | 102 | 101 | — | 101 |
| „ ( „ „ MeOH–$Me_2CO$) | 101 | — | 101 | 100 |

The slight over-estimation of chloride ion is just outside the error of the analytical method. It is due to a slow attack by silver salts on the complex cation, as was established by over-titrating, and then noting the slow disappearance of silver ion as indicated by the falling electromotive force. The over-estimation is smaller at later times than at earlier, because a product of the isomerisation which accompanies the rotation loss, the *trans*-dichlorocobalt(III) cation (see Part III, following paper) reacts with silver ion more slowly than does the original *cis*-isomer. The over-estimation is also reduced by titrating in acetone, because the responsible reaction is retarded by acetone, as we should expect from the theory of kinetic solvent effects for a reaction between two ions of like charge (Hughes and Ingold, *J.*, 1935, 252; Cooper, Dhar, Hughes, Ingold, MacNulty, and Woolf, *J.*, 1948, 2043).

The conclusion to be drawn from the analyses illustrated is therefore that appreciable chloride is not liberated from the complex cation either during or after the rotation loss.

(*2c*) *Chlorine Exchange between Chloride Ion and the Dichlorocobalt*(III) *Cation.*—No kinetically followed halogen exchange in co-ordination compounds seems to have been reported in the literature, though Grinberg observed very rapid exchange of bromine with a platinum complex, while Ettle and Johnson found no measurable exchange of chlorine with a cobalt complex in solution in water (cf. Section 2*b* of Part I).

The method of the present work was to add lithium radio-chloride to ordinary *cis*-dichlorobisethylenediaminecobalt(III) chloride in methyl alcohol, and, after various times at 35·8°, to chill samples to 0°, precipitate the chloride ion by the addition of a small excess of methyl-alcoholic silver nitrate at 0°, filter, and wash the precipitate quickly with a standard amount of ice-cold water, and measure the radioactivity of the combined filtrate made up to a standard volume.

The errors of the separation are (1) that a little covalently bound chlorine is pulled out of the complex cation by the silver salts, which are present in slight excess in order to ensure removal of all the anionic radioactivity, and (2) that a little of the complex cation remains adsorbed in the silver chloride. These errors were compensated when computing percentages of exchange at any finite time, by taking as the percentage for infinite time an experimental value determined by the same procedure. As two chlorine atoms are available to be exchanged, one-half of the value thus determined is the figure appropriate to represent equilibrium exchange with respect to one chlorine atom. This figure could be raised to 98% of the theoretical by using no excess of silver, but otherwise following our standard procedure for washing the silver chloride precipitate; but in fact it was kept slightly below the value stated by the employment of a definite small excess of silver.

We dealt with the complications that exchange of the second chlorine atom will overlap that of the first, and that the isomeric product of exchange, the *trans*-dichloro-cation (see

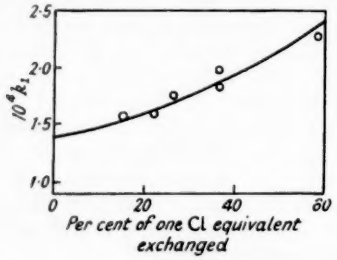



FIG. 2. *Mean specific rate of chlorine exchange between radio-*$Cl^-$ *and* $[Co\ en_2Cl_2]^+$ *as a function of the percentage progress of exchange; in* MeOH *at* 35·8°. (*Runs* 18 *and* 19.)

Part III) also contains exchangeable chlorine, by extrapolating mean specific rates, as measured at various stages of the exchange, back to yield the initial specific rate. This extrapolation also eliminated the need to correct for the gradual dilution, as exchange proceeded, of the supplied radio-chloride ion by produced ordinary chloride ion, though actually the degree of radioactive dilution was rendered nearly negligible by the use of lithium radio-chloride in large excess.

The extrapolation for runs (nos. 18 and 19) conducted at 35·8° and an ionic strength $\mu = 0{\cdot}040$ is shown in Fig. 2. The resulting value for the first-order rate-constant of exchange of the first chlorine atom, as measured by the radioactivity method, together with the estimated error, is entered as $k_1^{\text{rad-Cl}}$ below. The value of the polarimetric rate-constant under corresponding conditions, $k_1^{\text{pol-Cl}}$, along with the estimated error, is given for comparison (cf. Fig. 1):

$10^4 k_1^{\text{rad-Cl}}$, with $k_1^{\text{rad-Cl}}$ in sec.$^{-1}$ (35·8°, $\mu = 0{\cdot}040$, MeOH) $= 1{\cdot}4 \pm 0{\cdot}1$
$10^4 k_1^{\text{pol-Cl}}$, „ $k_1^{\text{pol-Cl}}$ „ „ „ $= 1{\cdot}35 \pm 0{\cdot}03$

We conclude that in principle the rates are identical.

### (3) *Action of Thiocyanate Ion on the* cis-*Dichloro-cation.*

(3*a*) *Polarimetric Study of Rate of Displacement of Chlorine by the Thiocyanate Ion.*—When a solution of lithium thiocyanate is added to one of the dichlorocobalt(III) chloride in methyl alcohol, substitution takes place, as is evident from the gradual colour change, and from analysis of the final product. Actually the substitution goes through two stages, though the second is considerably slower than the first:

$$[Co\ en_2Cl_2]^+ \xrightarrow{NCS^-} [Co\ en_2Cl(NCS)]^+ + Cl^- \xrightarrow{NCS^-} [Co\ en_2(NCS)_2]^+ + 2Cl^-$$

If the displacement of chlorine from the cation by thiocyanate ion in the first of these substitutions took place any faster than chlorine is displaced by chloride ion, or than optical activity is lost by the cation in the absence of thiocyanate ion, then we should be able to observe the increased rate through the rotation change, and also in other ways to be mentioned later.

The method of examining this question through the rotation change will be clear from the curves, shown in Fig. 3, for the optical rotation spectra in methyl alcohol of the *cis*-dichlorocobalt(III) ion and the *cis*-chlorothiocyanatocobalt(III) ion. In each case the isomer represented is that which Werner called *l*-; it is also the isomer which gives the less water-soluble (+)-α-bromocamphor-π-sulphonate. It will be seen that at λ 5893 Å, the mean wave-length of the sodium yellow doublet, the rotation of the optically active chlorothiocyanato-ion is not significantly different from zero. It follows that, when one thiocyanato-group replaces one chlorine atom in the original dichloro-cation, then the product, no matter which isomers are formed, whether *d-cis-*, *l-cis-*, *dl-cis*, or *trans-*, will, at this wave-length, have the rotation zero. At the same wave-length, the rotation of the original *l-cis*-dichloro-cation is large. Therefore any substitution by thiocyanate ion, at a rate exceeding that at which optical activity is lost from the dichloro-cation in the absence of thiocyanate ion, should show itself as an increased rate of loss of rotation at the stated wave-length.

The measurements made on these principles were not of high accuracy, because the small solubility of *l-cis*-dichlorobisethylenediaminecobalt(III) thiocyanate limited the available concentration of the dichloro-cation, and because the high absorptive power for Na-*D* light of the formed chlorothiocyanato-ion reduced the intensity of the transmitted light. However, over the first 60% of reaction, which is as much as could be followed owing to the increasing light absorption, and to within the error of the observations, the reaction followed a first-order rate-law; and the rate constants, given in Table 4, were

TABLE 4. *Rates of loss of optical activity from solutions of* $[Co\,en_2Cl_2]^+Cl^-$ *and* LiNCS *in* MeOH *at* 35·8°.

| Run No. | 20 | 21 | 22 |
|---|---|---|---|
| $[\{Co\,en_2Cl_2\}^+Cl^-]$ (mmole/l.) | 0·72 | 0·67 | 0·67 |
| [LiNCS] (mmole/l.) | 13·7 | 30·0 | 49·7 |
| $10^3\mu$ ($\mu$ = ionic strength) | 14 | 31 | 50 |
| $[NCS^-]/[\{Co\,en_2Cl_2\}^+]$ | 19 | 45 | 76 |
| $10^4k_1^{pol\cdot NCS}$ (with $k_1$ in sec.$^{-1}$) | 1·10 | 1·20 | 1·35 |

almost the same, for the same temperature and ionic strength, as the rate constants for rotation loss by the dichloro-cation when the only anion present was chloride ion (see Fig. 1). As Table 4 shows, the reaction with thiocyanate ion, though of first order overall, is of zeroth order with respect to thiocyanate ion: the thiocyanate ion was always held in large excess, but an increase by 3½ times in its concentration only slightly increased the rate. This slow increase of rate with ionic strength is quite similar to that observed for the rotation loss of the cation when chloride ion was the only anion (Section 2*a*).

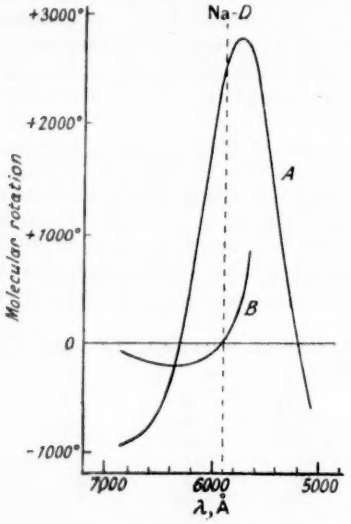
In order to simplify the foregoing account, we have anticipated the conclusion, for which we must now give the evidence, that the chemical process accompanying the loss of optical activity from the dichloro-cation in the presence of thiocyanate ion is essentially a substitution of bound chlorine by the thiocyanato-group.

(3*b*) *Spectrophotometric Study of the Displacement of Chlorine by the Thiocyanate Ion.*—For the above-described polarimetric experiments, solutions of the dichloro-cation were prepared with the aid of its chloride, rather than its thiocyanate, because of the readier solubility of the former salt, and because chloride ion was in any case going to be produced. However, thiocyanate ion was supplied in large excess over chloride ion, in order to ensure that nearly all the substitution would be effected by the thiocyanate ion. The colour change made it obvious that such substitution was concerned with the rotation loss. But in order to determine whether this was substantially the sole chemical process, it was necessary to examine the rate of change of some variable which would distinguish thiocyanate substitution from chloride exchange.

It was not found possible chemically to follow the liberation of chloride ion, because, as in aqueous solution (Werner, *Annalen*, 1912, **386**, 53), so in methyl-alcoholic solution, silver ion combines with complex cobalt ions containing a bound thiocyanato-group. Therefore we employed a spectrophotometric method, a chemical check being made on the end-product of substitution.

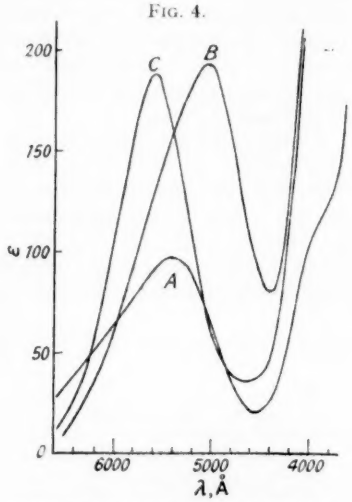
The principle of the method can be followed from Fig. 4, which records the absorption spectra, in methyl-alcoholic solution, of the *cis*-dichloro-cation, and of prepared samples of the *cis*- and *trans*-forms of its monosubstitution product, the chlorothiocyanato-cation. At λ 5400 Å the two chlorothiocyanato-isomers have the same extinction coefficient, which is considerably larger than that of the dichloro-compound. Therefore, by following the increase in absorption at this wave-length, we can observe the rate of introduction of the thiocyanato-group, independently of where it enters the complex.

FIG. 3.




*Rotatory dispersion of*:
$A$ = $[Co\ en_2Cl_2]^+Cl^-$,
$B$ = $[Co\ en_2Cl(NCS)]^+ClO_4^-$,
*in methyl alcohol at* 0°.

FIG. 4.




*Absorption spectra in methyl alcohol*:
$A$ = *cis*-$[Co\ en_2Cl_2]^+Cl^-$,
$B$ = *cis*-$[Co\ en_2Cl(NCS)]^+$ *bromocamphor-sulphonate*$^-$,
$C$ = *trans*-$[Co\ en_2Cl(NCS)]^+NCS^-$.

Actually the optical density, starting from the value for *cis*-$[Co\ en_2Cl_2]^+$, did not stop increasing when the value appropriate to $[Co\ en_2Cl(NCS)]^+$ was reached, because a second stage of substitution supervened with the production of still more strongly absorbing ions $[Co\ en_2(NCS)_2]^+$; and when, finally, a steady optical density was attained, a red salt whose analysis agreed with the formula $[Co\ en_2(NCS)_2]^+NCS^-$, could be isolated by precipitation with ether. However, at 35·8°, the time of half-conversion in the first substitution was about 2 hours, and in the second about 12 hours. Therefore we could obtain the specific rate of the first substitution from measured mean specific rates of change of optical density, from that of $[Co\ en_2Cl_2]^+$ towards that of $[Co\ en_2Cl(NCS)]^+$ at small degrees of conversion, the final step being to extrapolate to the limit of low conversions.

The extrapolations reveal what we interpret as a mass-law retardation, quite similar to that found (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979) for the unimolecular hydrolysis of benzhydryl (diphenylmethyl) halides: owing to the reversibility of the initial heterolysis, the developed chloride ion returns to the cation from which it separated to an increasing degree as reaction progresses, thereby retarding the thiocyanate substitution, even though this eventually proceeds to completion. The retardation is illustrated in Fig. 5. It is found, consistently with this interpretation, that as the initial

excess of thiocyanate ion is increased, the progressive retardation is lessened, until it becomes inappreciable at the largest excesses employed.

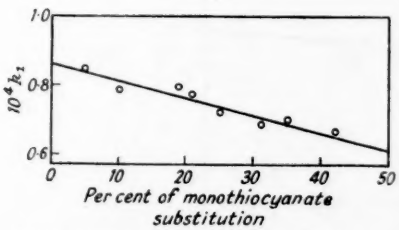
The extrapolated initial specific rates of substitution by the thiocyanate ion in the dichloro-cation, as determined by this method, are given in Table 5. As in these experi-

TABLE 5. *Spectrophotometrically measured rate of substitution by* $NCS^-$ *in cis-*$[Co\ en_2Cl_2]^+$ *to give* $[Co\ en_2Cl(NCS)]^+$ *in* MeOH *at* 35·8°.

| Run No. | 23 | 24 | 25 | 26 |
|---|---|---|---|---|
| $[\{Co\ en_2Cl_2\}^+Cl^-]$ (mmole/l.) | 0·72 | 0·71 | 0·67 | 0·67 |
| [LiNCS] (mmole/l.) | 13·7 | 15·6 | 30·0 | 49·7 |
| $10^3\mu$ ($\mu$ = ionic strength) | 14 | 16 | 31 | 50 |
| $[NCS^-]/[Cl^-]$ | 19 | 22 | 45 | 74 |
| $10^4k_1^{phot\text{-}NCS}$ (with $k_1$ in sec.$^{-1}$) | 0·78 | 0·87 | 1·13 | 1·30 |

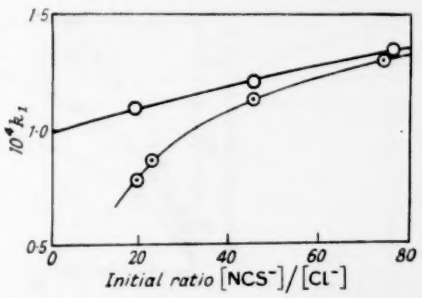
ments some chloride ion is present initially, the mass-law effect should reduce the spectrophotometrically measured initial rates, below the polarimetric rates reported in the preceding Section, which refer strictly to total rates of substitution by thiocyanate ion plus chloride ion. However, as the excess of thiocyanate is increased, the spectrophotometric rate should converge on the polarimetric rate, even though both rates are being increased by the increasing ionic strengths of the solutions. All this happens, as is illustrated in Fig. 6. Evidently the polarimetric rate is equal to the rate of substitution by thiocyanate ion, when this is the only substitution taking place, just as the same polarimetric rate is equal to the rate of substitution by chloride ion when that is the sole form of substitution.*

FIG. 5.




*Spectrophotometric rate of substitution in* cis-$[Co\ en_2Cl_2]^+$ *by* $NCS^-$ *in* MeOH *at* 35·8°, *showing progressive retardation by mass-law effect of developing chloride ion.* (*Run* 24.)

FIG. 6.




*Rates of substitution in* cis-$[Co\ en_2Cl_2]^+$ *by* $NCS^-$ *in* MeOH *at* 35·8°.

○ Polarimetric rates (substitution by $NCS^-$ plus $Cl^-$)

○ Initial spectrophotometric rates (substitution by $NCS^-$ only).

(4) *Action of Azide Ion on the* cis-*Dichloro-cation.*

(4*a*) *Study by Potentiometric Titration of the Rate of Displacement of Chlorine by the Azide Ion.*—The reaction between azide ion and the dichlorocobalt(III) cation proceeds through two stages of substitution :

$$[Co\ en_2Cl_2]^+ \xrightarrow{N_3^-} [Co\ en_2ClN_3]^+ + Cl^- \xrightarrow{N_3^-} [Co\ en_2(N_3)_2]^+ + 2Cl^-$$

When slightly more than one molecular proportion of azide ion is supplied, the first stage of substitution goes practically to completion, giving no indication of appreciable rever-

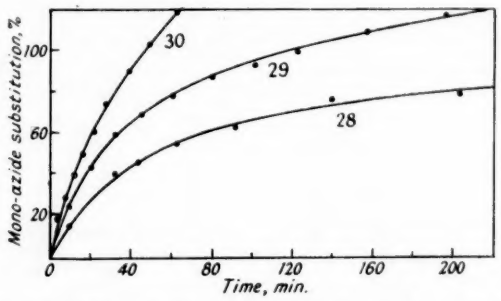
* It should be noted that the mass-law effect on rate of substitution by thiocyanate would be over-estimated if we should compute it directly from the proportional separation of the two curves in Fig. 6. This is because substitution in the dichloro-cation by chloride ion does not leave the optical density unchanged, but reduces it. For, as will be noted in Part III, this substitution in the *cis*-cation is associated with partial conversion into the *trans*-isomer, which is less light-absorbing at the wave-length here employed. However, the comparison in the text is still correct, because, as the mass-law retardation tends to zero with increasing excess of thiocyanate ion, so the expected over-estimation tends to zero; and thus the curves of Fig. 6 should still coalesce at high excesses of thiocyanate.

sibility. With excess of azide ion the successive stages of substitution occur, overlapping in time, though the second stage is sufficiently slower than the first to enable approximate rate constants to be calculated for the first stage, with neglect of the second, from measurements made over the first 70% of the first stage.

The kinetics of the substitution have been followed by potentiometric titration of the liberated chloride ion. That they are different from the kinetics of the substitutions already discussed will be clear from the curves in Fig. 7, which show the course of azide substitutions in the initial presence of slightly more than one, slightly more than two, and a little less than three azide ions to one complex cobalt ion. Evidently the rate of substitution depends on the concentration of the entering azide ion.

The results of a closer analysis of the data are given in Table 6. When we try to compute first-order rate constants the values drift; but if, nevertheless, we calculate mean first-order constants for the first 70% of reaction, these values, instead of being the same in the various runs, rise approximately in proportion to the initial concentrations of azide ion (line 4). If, guided by this result, we compute mean second-order constants for the first 70% of reaction, the values are nearly the same for the different runs (line 5).

FIG. 7.




*Rates of substitution in* cis-$[Co\ en_2Cl_2]^+$ *by* $N_3^-$ *in* MeOH *at* 35·8°.

(28) *Initially* $[Co\ en_2Cl_2]^+$ 0·94, $N_3^-$ 1·04 *millimolar.*
(29) ,, ,, 0·82, ,, 1·72 ,,
(30) ,, ,, 0·80, ,, 2·21 ,,

However, there are still appreciable drifts, indicating roughly compensatory disturbances, some of which, including the incursion of a second stage of substitution, we can eliminate by an extrapolation to give initial second-order rates. The resulting values (line 6) are not quite the same in the different runs. But we can calculate that they represent rates

TABLE 6. *Titrimetrically measured rates of substitutions by* $N_3^-$ *in cis-*$[Co\ en_2Cl_2]^+$ *to give* $[Co\ en_2ClN_3]^+$ *in* MeOH *at* 35·8°.

| | | | |
|---|---|---|---|
| (1) Run No. | 28 | 29 | 30 |
| (2) $[\{Co\ en_2Cl_2\}^+Cl^-]$ (mmole/l.) | 0·94 | 0·82 | 0·80 |
| (3) $[NaN_3]$ (mmole/l.) | 1·04 | 1·72 | 2·21 |
| (4) $10^4k_1$ ($k_1$ in sec.$^{-1}$; first 70% reaction) | 3·22 | 5·33 | 7·07 |
| (5) $k_2$ (sec.$^{-1}$ mole$^{-1}$ l.; first 70% reaction) | 0·31 | 0·31 | 0·32 |
| (6) $k_2$ (sec.$^{-1}$ mole$^{-1}$ l.; initial rate) | 0·34 | 0·31 | 0·29 |
| (7) $k_2$ (initial; corr. for unimolecular process) | 0·24 | 0·25 | 0·25 |
| (8) $k_2^{anal\text{-}N_3}$ (sec.$^{-1}$ mole$^{-1}$ l.) (best value) | 0·26—0·27 | | |

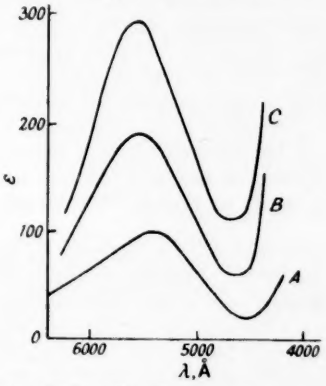
only 3—6 times greater than the rate of the uniform first-order reaction of the dichloro-cation, which we measured by its rotation loss, and also by its substitution with chloride ion, and with thiocyanate ion, and must expect to find as a constituent of the reaction with azide ion. It is easy to make an upper-limiting correction for this first-order process, by assuming that every one of the molecular acts composing it introduces an azido-group, and that none exchanges chlorine, or, in other words, that the mass-law retardation by chloride ion of unimolecular azide substitution is negligible. Thus corrected, the second-

order rate constants become constant among the runs (line 7). The over-correction will, of course, become less as larger initial concentrations of azide ion diminish the mass-law retardation of the unimolecular part of the reaction. It follows that the true second-order rate constant can be estimated by extrapolation to high azide concentrations: an estimate on this basis is given (line 8). In practice we were prevented from employing very large excesses of azide ion by the low solubility of the azides of the complex cations.

Examination of the kinetics at 25·9° led to an uncorrected initial $k_2$ of 0·112 sec.$^{-1}$ mole$^{-1}$ l., and a maximally corrected value 0·096 sec.$^{-1}$ mole$^{-1}$ l. If we take, as the best estimate for this temperature, the value 0·100 sec.$^{-1}$ mole$^{-1}$ l., then this, along with the figure for 35·8° given in Table 6, leads to an Arrhenius energy of activation of 18 kcal./mole for the second-order substitution by azide ion. An approximate knowledge of the temperature coefficient of this reaction is useful in connexion with a comparison of rates made later.

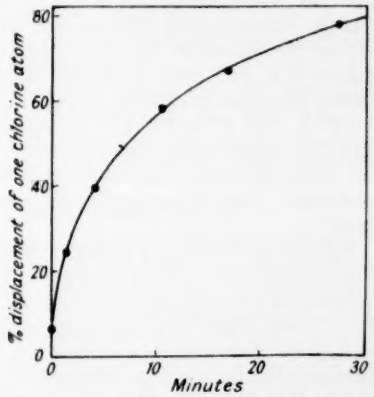
(4*b*) *Changes in Absorption during the Displacement of Chlorine by Azide Ion.*—The curves of Fig. 8 show the changes in light absorption which accompany substitution of

FIG. 8. *Absorption spectra during azide substitution.*




*Run* 30 (*see Fig.* 7):
*A, at time zero. B, at time* 100 *min. C, at time* 24 *hr.*

FIG. 9.




*Substitution in* cis-$[Co\ en_2Cl_2]^+$ *by* $MeO^-$ *at* 0°. (*Run* 33.)

the chlorine in the *cis*-dichlorobisethylenediaminecobalt(III) ion by azido-groups. The lowest curve applies to the original cation $[Co\ en_2Cl_2]^+$, and the uppermost curve to its final substitution product $[Co\ en_2(N_3)_2]^+$, the stereochemical form of which is not yet known, though one salt of this composition has been described (Strecker and Oxenius, *Z. anorg. Chem.*, 1934, **218**, 151). We have not yet studied the intermediates $[Co\ en_2ClN_3]^+$ in isolation.

(5) *Action of Methoxide and Hydroxide Ions on the* cis*-Dichloro-cation.*

(5*a*) *Displacement of Chlorine in Methyl-alcoholic Sodium Methoxide.*—An attempt has been made to study the rate of the first of the two possible substitutions,

$$[Co\ en_2Cl_2]^+ \xrightarrow{OMe^-} [Co\ en_2Cl(OMe)]^+ + Cl^- \xrightarrow{OMe^-} [Co\ en_2(OMe)_2]^+ + 2Cl^-$$

The reaction is not well adapted for quantitative investigation, but even our qualitative or semi-quantitative results are significant in relation to the general pattern of kinetic data recorded in this paper. The difficulties in the way of quantitative study are, first, that it was not found possible to employ the methyl-alcoholic solvent in so dry a state that our small concentrations of alkali could with certainty be regarded as methoxide ion entirely, without any hydroxide ion; and secondly, that even at 0° the substitution was inconveniently fast for the analytical method.

The methyl-alcoholic solvent, though carefully dried before use, could have acquired

between 0·01 and 0·1% of water by the time the manipulations involved in its employment were completed. Theoretically this could allow from about 5 to 45% of the introduced methoxide ion to suffer conversion into hydroxide ion, and thus to lead to a hydroxy-substitution product in place of the wanted methoxy-substitution product. If the much greater complexing power of water than of methyl alcohol provides a reliable analogy, we might expect the hydroxy-substitution product to be formed, in place of the methoxy-substitution product, nearly to the stoicheiometrically permitted extent.

Owing to the great rates of substitution, we employed about millimolar concentrations, and worked at 0°. Our lack of knowledge of the physical properties of the substitution products precluded the use of physical methods of following the kinetics. The disappearance of alkali was not followed directly, because the substitution products themselves are bases. Therefore we used potentiometric titration of the liberated halide ion. However, as the process of substitution had to be stopped by destroying the substituting agent with acid and as the substitution products were unstable in acid, as will be noted below, the analytical procedure, despite the utmost expedition and the use of low temperatures, was inexact.

Part of the evidence that both hydroxy- and methoxy-substitution products are formed is that, when a small amount of water was deliberately added to the methyl alcohol, then a large proportion of chlorine was liberated instantaneously, whilst any remaining chlorine was thereafter set free in a reaction having a rate of the order of magnitude of that observed in the most carefully dried solvents. With well-dried solvents the instantaneous liberation of chloride ion could be cut down to small proportions, as illustrated for Run 33 in Fig. 9, while the kinetically followed liberation pursued a course, which, to within the considerable experimental error, could be represented as a second-order reaction. The high rate itself shows that the rate depends on the anion, as well as on the dichloro-cation. For the second-order rate constant at 0° we find $k_2^{\text{anal-OMe}} = 1{\cdot}8 \pm 0{\cdot}2$ sec.$^{-1}$ mole$^{-1}$ l.

(5*b*) *Effect of Acid on the Product of Methoxide Substitution.*—In an attempt to discover something of the properties of the cation $[Co\ en_2Cl(MeOH)]^{++}$, a methyl-alcoholic solution of the product of a methoxide-ion substitution was acidified with methyl-alcoholic hydrogen chloride. It was found that one equivalent of chloride ion rapidly disappeared from the solution: more than half of this one equivalent had gone before the first measurement could be made, while the rest disappeared more gradually, sufficiently so to suggest that the solution before acidification contained two acid-sensitive products (Run 35). It is a surmise that the cation formulated above accepts chlorine in place of methyl alcohol very quickly, while the aquo-cation $[Co\ en_2Cl(H_2O)]^{++}$ undergoes an analogous displacement of water more slowly. Contemporaneously with these effects, a slow change commenced in the colour of the solution, which changed from violet to green. The final green product was shown by its absorption spectrum to be *trans*-$[Co\ en_2Cl_2]^+$. The following scheme is consistent with these observations:

$$[Co\ en_2Cl(OMe)]^+ \xrightarrow[\text{fast}]{H^+} [Co\ en_2Cl(MeOH)]^{++} \xrightarrow[\text{fast}]{Cl^-}$$

$$\textit{cis}\text{- and }\textit{trans}\text{-}[Co\ en_2Cl_2]^+ \xrightarrow[\text{slow}]{} \textit{trans}\text{-}[Co\ en_2Cl_2]^+$$

(6) *Action of Nitrate Ion on the* cis*-Dichloro-cation.*

A brief polarimetric study has been made of the action of nitrate ions, introduced mainly as lithium nitrate, on the *cis*-dichlorobisethylenediaminecobalt(III) ion, introduced as its nitrate, in solvent methyl alcohol. In these conditions chloride ion was liberated, but a large excess of nitrate ion was always present. The colour changes are instructive. When chloride ion is the only anion acting on the violet *cis*-dichloro-cation, then the final product is the green *trans*-dichloro-cation. However, in the initial presence of excess of nitrate ions, the final product is purple-red. This can only be due to the formation of $[Co\ en_2Cl(NO_3)]^+$ or $[Co\ en_2(NO_3)_2]^+$. Accompanying this change of colour, there is a loss of optical rotation, closely similar to that which accompanies substitution by chloride ion or by thiocyanate ion (Sections 2*a* and 3*a*). The rotation loss accompanying the nitrate

reaction is of first order in the dichloro-cation, and of zero order in nitrate ion. It shows the same slow increase with ionic strength, as that already described in connexion with substitution by chloride ion, and by thiocyanate ion. Furthermore, as far as the conditions allow comparison, the absolute rate of the first-order polarimetric change accompanying nitrate substitution is the same as the corresponding rates for the chloride and thiocyanate substitutions (cf. Fig. 1). The figures are in Table 7. The comparison of

TABLE 7. *Rates of loss of optical activity from solutions of* $[Co\,en_2Cl_2]^+NO_3^-$ *and* $LiNO_3$ *in* MeOH *at* 35·8°.

| Run No. | 36 | 37 | 38 | 39 | 40 |
|---|---|---|---|---|---|
| $[\{Co\,en_2Cl_2\}^+NO_3^-]$ (mmole/l.) | 0·73 | 0·75 | 1·47 | 1·49 | 0·74 |
| $[LiNO_3]$ (mmole/l.) | 9·2 | 43·4 | 312 | 733 | 367 |
| [LiCl] (mmole/l.) | — | — | — | — | 350 |
| $10^3\mu$ ($\mu$ = ionic strength) | 10 | 44 | 313 | 734 | 717 |
| $[NO_3^-]/[\{Co\,en_2Cl_2^+\}]$ | 14 | 59 | 213 | 492 | 497 |
| $[Cl^-]/[\{Co\,en_2Cl_2^+\}]$ | — | — | — | — | 473 |
| $10^4k_1^{pol\text{-}NO_3}$ (with $k_1$ in sec.) | 1·15 | 1·37 | 1·68 | 1·87 | 1·91 |

absolute rates cannot be made quite precise, because in these experiments 0·5% of water was added to the methyl alcohol in order to avoid difficulties due to low solubility of some of the nitrates in dry methyl alcohol. However, the comparison between the last two experiments noted in Table 7 is straightforward. The ionic strengths are nearly the same, but in one of the experiments about half the nitrate ion present in the other has been replaced by chloride ion. In the experiment with added nitrate only, the final colour was purple-red. In the experiment with both nitrate and chloride, the final colour was an impure, very pale green. Evidently in this experiment there has been substitution by both nitrate and chloride. Yet the rates in the two experiments are practically identical.

### (7) *Action of Bromide Ion on the* cis-*Dichloro-cation.*

A similar short study has been made of the action of bromide ions introduced as lithium bromide, on the dichloro-cation, introduced as nitrate, the conditions being the same as in the experiments described in the immediately preceding Section. Chlorine is liberated as chloride ion, and bromine enters the complex. The solution changes colour from violet to yellow-green, which is the colour of *trans*-$[Co\,en_2ClBr]^+$. Accompanying this bromide substitution there is a loss of optical rotatory power closely similar to that which accompanies substitutions by chloride, thiocyanate, and nitrate ions. It is of first order in the complex cation, but of zero order in bromide ion. It shows the usual positive salt effect. As far as comparison is possible its absolute rate is the same as that associated with the other substitutions mentioned (cf. Fig. 1). The figures are in Table 8.

TABLE 8. *Rate of loss of optical activity from solutions of* $[Co\,en_2Cl_2]^+NO_3^-$ *and* LiBr *in* MeOH *at* 35·8°.

| Run No. | 41 | 42 | 43 |
|---|---|---|---|
| $[\{Co\,en_2Cl_2\}^+NO_3^-]$ (mmole/l.) | 1·77 | 1·78 | 1·83 |
| [LiBr] (mmole/l.) | 2·76 | 10·4 | 57·5 |
| $10^3\mu$ ($\mu$ = ionic strength) | 3·5 | 12 | 59 |
| $[Br^-]/[\{Co\,en_2Cl_2\}^+]$ | 1·6 | 5·8 | 31·4 |
| $10^4k_1^{pol\text{-}Br}$ (with $k_1$ in sec.$^{-1}$) | 1·08 | 1·20 | 1·52 |

### (8) *Action of Nitrite Ion on the* cis-*Dichloro-cation.*

We have made a short examination of the action of nitrite ions introduced as sodium nitrite, on the *cis*-dichloro-cation, introduced in the form of its nitrate, the conditions being as in the experiments of the two immediately preceding Sections. It emerged that this substitution by nitrite ion is mechanistically marginal, and has a mixed kinetic form. Having observed this, we did not pursue the matter closely, since a quantitative kinetic analysis would have involved much detailed work, and it seemed that the qualitative deduction from the experiments mentioned was likely to be the most interesting of any conclusions that a comprehensive study might have yielded.

When nitrite ion acts on the dichloro-cation in methyl alcohol, chloride ion is liberated,

and nitrite ion enters the complex, to form, finally, dinitro-cations. The colour changes from violet to golden-yellow. Solutions of both *cis*- and *trans*-$[Co\ en_2(NO_2)_2]^+$ are yellow. The substitution is accompanied by a first-order loss of optical rotation, which, however, is dependent (apart from salt effects) on the concentration of nitrite ion. By the use of high proportions of nitrite ions, the rates are raised considerably above the first-order rate associated, at given ionic strength, with substitutions by chloride, thiocyanate, nitrate, and bromide ion. The illustration in Table 9 is an extreme one, in which, by the use of a 300-fold excess of nitrite ion, the rate is built up to 3·5 times the common first-order rate at the same ionic strength, of any of the substitutions mentioned. We assume the incursion, in general of some, and in this example of a predominating amount, of bimolecular substitution by nitrite ion. Such substitution would produce an increased rate of loss of optical activity whether the immediate bimolecular product were the *trans*-, the racemic *cis*-, or an optically active *cis*-form of $[Co\ en_2Cl(NO_2)]^+$, because the last has only a small rotatory power for yellow light relatively to that of the original dichloro-compound. By neglecting the possible small rotatory power of the bimolecular product, we can, after making an estimated allowance for the part of the rate which does not depend on nitrite ion, compute an approximate value for the second-order rate of substitution by nitrite ion, as is done in Table 9.

TABLE 9. *Rate of loss of optical activity from a solution of* $[Co\ en_2Cl_2]^+NO_3^-$ *and* $[NaNO_2]$ *in* MeOH *at* 35·8°. (*Run* 45.)

| | |
|---|---|
| $[\{Co\ en_2Cl_2\}^+NO_3^-]$ (mmole/l.) | 0·576 |
| $[NaNO_2]$ (mmole/l.) | 165 |
| $10^4k_1^{pol\text{-}NO_2}$ (composite) ($k_1$ in sec.$^{-1}$) | 6·0 |
| $10^4k_1^{pol\text{-}NO_2}$ (estimated unimolecular part) | 1·7 |
| $k_2^{pol\text{-}NO_2}$ (sec.$^{-1}$ mole$^{-1}$ l.) (by difference) | 0·0026 |

(9) *Discussion: The Two Mechanisms of Substitution.*

We have now described nucleophilic substitutions by seven anions each displacing chlorine from the *cis*-dichlorobisethylenediaminecobalt(III) ion in solvent methyl alcohol. For four of these anionic reagents, the nitrate, chloride, bromide, and thiocyanate ion, substitution proceeds according to a first-order law: the rates depend on the concentration of the cation undergoing substitution, but not on that of the substituting agent; and thus the rates are the same for all these substituting agents (the medium and temperature being the same), as shown by the graphical conspectus in Fig. 1. This common rate is also the rate at which the cobalt cation loses optical activity in the absence of any stronger nucleophilic reagent than those mentioned. We interpret these reactions as unimolecular nucleophilic substitutions, involving loss of asymmetry in the rate-determining solvent-assisted dissociation:

$$[Co\ en_2Cl_2]^+ \xrightarrow{\text{slow}} \underset{\text{(optically inactive)}}{[Co\ en_2Cl]^{++}} \xrightarrow[X^-]{\text{fast}} [Co\ en_2ClX]^+ \quad . \ . \ . \ . \ . \quad (S_N1)$$

Certain detailed kinetic observations fit this interpretation. An ionic-strength acceleration of the somewhat large order of magnitude of those observed in organic unimolecular substitutions has been found; and a mass-law retardation, which, when it can be observed, is the most diagnostic kinetic character of the unimolecular mechanism, has been observed in these substitutions.

Three of the anionic reagents substitute partly or wholly according to a second-order law. Substitution by nitrite ion shows mixed kinetics, but a considerable part of the rate may depend on the concentration of the anions. The faster substitution by azide ion proceeds mainly according to a second-order law, the rate depending not only on the cation substituted but also on the substituting agent, though a small background reaction of first-order form appears to be present. The still faster substitution by methoxide ion follows a second-order law, as closely as could be ascertained in face of difficulties due to the high rate. We interpret these second-order reactions as bimolecular nucleophilic substitutions:

$$X^- + [Co\ en_2Cl_2]^+ \longrightarrow [Co\ en_2ClX]^+ + Cl^- \quad . \ . \ . \ . \ . \quad (S_N2)$$

The second-order substitutions differ so widely with respect to rate that they could not all be kinetically investigated at the same temperature. However, having determined the temperature coefficient of the rate of the azide substitution, we can compare this rate, on the one hand, with that of the nitrite substitution at 35·8°, and, on the other, with that of the methoxide substitution at 0°. We thus estimate that, at a common temperature, the second-order rates of reaction of the three substituting agents, $OMe^-$, $N_3^-$, $NO_2^-$, would stand approximately in the ratio 30,000 : 100 : 1.

These relations show that the second-order reactions are not conjugate-base substitutions $S_N1cB$ or $S_N2cB$, rate-controlled by the extraction of a proton from an ethylenediamine ligand. If they were, the rates would depend on the basicity of the reagent, not on nucleophilic power apart from this specific form. We should expect to be able to make a Brönsted plot, demonstrating a linear free-energy relation between rate and basicity. Now $OMe^-$ is more basic than $N_3^-$ by a ratio of something like $10^{12}$, while $N_3^-$ is more basic than $NO_2^-$ by one of only about $10^{1.5}$. These factors bear no kind of linear-logarithmic relation to the rate ratios, $10^{2.5}$ from $OMe^-$ to $N_3^-$, and $10^2$ from $N_3^-$ to $NO_2^-$. Obviously these reagents are not attacking a proton, and therefore they must be attacking the cobalt atom, as assumed in our interpretation of the reactions as $S_N2$ substitutions.

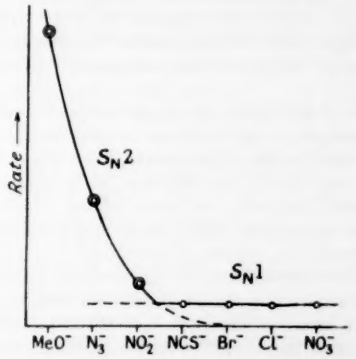



FIG. 10.

*Summary of kinetic relations applying to nucleophilic substitution in* cis-$[Co\ en_2Cl_2]^+$. (*Schematic.*)

Our mechanistic deductions have support from analogy; for the kinetic situation is not unprecedented. It was shown in 1935 for nucleophilic substitution at carbon, that, if substituting agents, arranged in order of diminishing nucleophilic power, are considered with respect to their substitutions in the same alkyl compound, then, on passage through the series, the reaction order at first remains second, while the absolute rates diminish strongly from case to case, until a point of change is reached, whereafter the reaction order becomes first, and the rates maintain a constant value in the successive cases. Gleave, Hughes, and Ingold represented these relations in a schematic diagram (*J.*, 1935, 236). Their conclusion, that the change of kinetic form, and of rate trend, betrays a change of mechanism from $S_N2$ to $S_N1$, is to-day well understood. The present study of nucleophilic substitutions at octahedrally bonded cobalt has revealed a similar pattern of results, which we may likewise represent schematically, as in Fig. 10. Our deduction concerning the co-existence of mechanisms $S_N2$ and $S_N1$ in this range of substitution is only an extension of the old conclusion; but we emphasise the extension, believing that the idea of duplexity of mechanism has a notable part to play in the future study of inorganic substitutions, just as it has been basic to the growth in recent decades of our knowledge of organic substitutions.

### (10) *Experimental Methods and Illustrative Data.*

(10*a*) *Preparations.*—*trans*-Dichlorobisethylenediaminecobalt(III) chloride was prepared and converted into the *cis*-isomer, and the latter was resolved through the (+)-α-bromocamphor-π-sulphonate, from which the optically active chloride was regenerated, essentially as described

in " Inorganic Syntheses," Vol. II, p. 222. For optical measurements the *trans*-isomer had to be freed from accompanying, less soluble, trisethylenediaminecobalt(III) chloride: this was accomplished by extracting the dichloro-salt with water, and, after filtering, causing it to crystallise by the addition of ethyl alcohol, and then extracting it with, and crystallising it from, dry methyl alcohol (Found: C, 16·9; N, 19·7; Cl, 37·1. Calc.: C, 16·8; N, 19·6; Cl, 37·3%). The *cis*-isomer, prepared from the crude *trans*-isomer, became purified during its resolution (Found, for the *l-cis*-bromocamphorsulphonate: N, 10·0. Calc.: N, 10·0%). The *l-cis*-chloride (Found: C, 16·8; N, 19·6%), freed from the bromocamphorsulphonate by treatment, repeated as necessary, with cold alcoholic-ethereal hydrogen chloride followed by alcohol, was converted into the nitrate (Section 6) by precipitation with lithium nitrate from methyl-alcoholic solution.

The *trans*-dichloro-chloride was converted by treatment with potassium thiocyanate into *trans*-chlorothiocyanatobisethylenediaminecobalt(III) thiocyanate and *cis*-chlorothiocyanatobis-ethylenediaminecobalt(III) chloride, and the latter was resolved to give the *l-cis*-chlorothiocyanato-(+)-α-bromocamphor-π-sulphonate, and thence the *l-cis*-chlorothiocyanato-perchlorate, essentially as described by Werner (*Annalen*, 1912, **386**, 133). For optical measurements the bromocamphorsulphonate was crystallised from methyl alcohol with addition of ether (Found: C, 30·6; N, 12·0. Calc.: C, 30·8; N, 12·0%). The *trans*-chlorothiocyanato-thiocyanate was purified by crystallisation from water (Found: C, 22·1; H, 4·8; N, 25·2. Calc.: C, 21·8; H, 4·9; N, 25·4%), and, by means of potassium iodide, was converted into the iodide, which was crystallised from water (Found: C, 14·9; N, 17·7. Calc.: C, 15·0; N, 17·5%). The dithiocyanato-thiocyanate was obtained as a final product of one of the investigated substitutions, as noted in Section 3*b* (Found: C, 24·2; H, 4·6. Calc.: C, 23·8; H, 4·6%).

Most of the required simple reagents were prepared or purified by standard methods. It was found more satistactory to prepare lithium thiocyanate from purified lithium sulphate and purified barium thiocyanate, than to try to purify commercial lithium thiocyanate. Methyl alcohol was dried by reaction with magnesium, and subsequent storage over magnesium perchlorate, followed by distillation. Lithium radio-chloride was prepared by a Szilard–Chalmers separation from potassium perchlorate, which had been irradiated for one month in the Harwell pile, under a flux of $10^{10}$ neutrons per cm.$^2$ per sec., and kept for a further month in order to allow decay of most of the potassium activity. To a solution of this material in water, a small amount of sodium chloride was added as carrier, and then the chloride was precipitated as silver chloride, converted by reduction with hydrogen at red heat into hydrogen chloride, and thence into lithium chloride, which was purified with the aid of acetone, and dried. Lithium chloride, both ordinary and radioactive, as well as other lithium salts, were stored in solution in dry methyl alcohol suitably protected in the reservoir of an automatic burette.

(10*b*) *Apparatus.*—Measurements of rotatory dispersion were made on a spectropolarimeter with monochromator by Schmidt and Haentsch. For polarimetrically-followed kinetic runs a polarimeter by Hilger (Mk. 11) was employed along with a sodium lamp. Both for measurements of absorption spectra, and for spectrophotometrically-followed kinetic runs, the Unicam quartz spectrophotometer (SP 500) was used. For measurements of radioactivity, a Geiger counter tube of type M6, by Twentieth Century Electronics, was employed, pulses from the counter being amplified and fed into a Morley and Duke scaling unit, there to be magnetically counted and recorded. The potentiometric titration equipment was standard.

(10*c*) *Polarimetric Kinetics.*—The first measurements of the rate of loss of optical activity from *cis*-dichlorobisethylenediaminecobalt(III) salts were made by maintaining the sample continuously in a jacketed polarimeter tube at the experimental temperature. However, it was discovered that the light passing through the polarimeter tube accelerated the reaction appreciably, and therefore all recorded runs of the final series were made by the following method which excludes the action of light.

The experimental solution was prepared, with the aid of solvent and salt solutions delivered from the automatic burettes, in a dry nitrogen-filled flask connected through a sealed-in sintered-glass filter to the dry nitrogen-filled reservoir of an automatic pipette, into which the solution was transferred by suction. From there it was delivered under nitrogen and sealed into ten tubes, which were cooled to −80°, blackened, and transferred to the blackened thermostat. After an allowance of 2 minutes for warming up, the first tube, representing the time zero of the kinetic run, was cooled to −80°, and at known subsequent times the other tubes were similarly cooled. For measurement of the optical rotations, the contents of each tube were transferred in turn to a jacketed polarimeter tube held at 0°. The change of rotation at this

temperature is too small to be observed in 30 minutes, and thus plenty of time was available for making the readings as precise as the equipment permitted. A sample run is recorded in Table 10.

TABLE 10. *Loss of optical rotation of l-cis-*$[Co\ en_2Cl_2]^+Cl^-$ *in* MeOH *at* 35·8° (*Run no.* 1.)

Initially $[\{Co\ en_2Cl_2\}^+Cl^-] = 1{\cdot}745 \times 10^{-3}$M; $\alpha$ = observed rotation in a 10-cm. tube at 0° for Na light; $k_1 = (2{\cdot}303/t)\log_{10}(\alpha_0/\alpha_t)$.

| $t$ (min.) | 0 | 16 | 38 | 58·5 | 77·5 | 103·5 | 146 | 187·5 | 249·5 |
|---|---|---|---|---|---|---|---|---|---|
| $\alpha$ (deg.) | 0·417 | 0·378 | 0·324 | 0·297 | 0·256 | 0·220 | 0·176 | 0·129 | 0·080 |
| % Reaction | 0 | 9·3 | 22·3 | 28·8 | 38·6 | 47·2 | 57·8 | 69·1 | 80·8 |
| $10^4k_1$ (min.$^{-1}$) | — | 61 | 66 | 58 | 63 | 62 | 59 | 63 | 66 |

Mean $k_1 = 0{\cdot}0063$ min.$^{-1}$.

(10*d*) *Spectrophotometric Kinetics.*—The optical density $\log_{10}(I_0/I) = \varepsilon cd$, where $I_0$ is the intensity of the incident and $I$ that of the emergent light, and $\varepsilon$ is the extinction coefficient, $c$ the concentration, and $d$ the cell thickness, has been used to follow, for example, the conversion of the dichloro-cation, through substitution by the thiocyanate ion, into the chlorothiocyanato-cation. Most of the optical-density measurements were made on the solution which had been used for the rotation measurements, some of the solution, still at 0°, being transferred to the absorption cell of the spectrophotometer. A specimen run is given in Table 11.

TABLE 11. *Change of optical density at* 5400 Å *during the reaction of cis-*$[Co\ en_2Cl_2]^+Cl^-$ *with* LiNCS *at* 35·8° *in* MeOH. (*Run no.* 23.)

Initially $[\{Co\ en_2Cl_2\}^+Cl^-] = 0{\cdot}718 \times 10^{-3}$M, and [LiNCS] $= 13{\cdot}7 \times 10^{-3}$M.
$D$ = optical density in a 4-cm. cell for $\lambda$ 5400 Å; $k_1 = (2{\cdot}303/t)\log_{10}(D_\infty - D_0)/(D_\infty - D_t)$.

| $t$ (min.) | 0 | 10·5 | 20 | 30 | 41·3 | 52·5 | 63·8 | 79 | 103·5 | 140 |
|---|---|---|---|---|---|---|---|---|---|---|
| $D_t$ | 0·277 | 0·286 | 0·292 | 0·300 | 0·306 | 0·314 | 0·322 | 0·331 | 0·341 | 0·355 |
| % Reaction | 0 | 5·0 | 8·3 | 12·6 | 15·9 | 20·3 | 24·8 | 29·7 | 35·1 | 42·9 |
| $10^4k_1$ (min.$^{-1}$) | — | 49 | 43 | 45 | 42 | 43 | 45 | 45 | 42 | 40 |

From absorption spectrum $D_\infty = 0{\cdot}459$. Extrapolated $k_1 = 0{\cdot}0047$ min.$^{-1}$.

(10*e*) *Kinetics of Chlorine Exchange by Radioactivity.*—A solution of weighed *cis*-dichlorobisethylenediaminecobalt(III) chloride in methyl alcohol was made up in the dry, nitrogen-filled reservoir of an automatic sampling apparatus, immersed in a darkened thermostat at 35·8°, and a known volume of methyl-alcoholic lithium radio-chloride was added. After 3 minutes the first measured sample, representing the time-zero of the kinetic run, was expelled into a cooled beaker, brought as quickly as possible to −20°, and treated with methyl-alcoholic silver nitrate in slight excess over the equivalent of the ionic chlorine. The solution was immediately filtered, and the precipitate quickly washed with ice-cold water, into a standard flask, and the filtrate, after the addition of a few drops of concentrated aqueous ammonia, was then made up to the volume mark. Counts were made on this solution at convenience. Other portions of solution from the sampling apparatus at known subsequent times were treated similarly. Because of the large excess of lithium chloride used, a first-order equation was applied. An illustrative run is recorded in Table 12.

TABLE 12. *Exchange of chlorine between cis-*$[Co\ en_2Cl_2]^+$ *and* $Cl^-$ *in* MeOH *at* 35·8°. (*Run no.* 18.)

Initially $[\{Co\ en_2Cl_2\}^+Cl^-] = 1{\cdot}77 \times 10^{-3}$M; [$^{36}$Cl-labelled LiCl] $= 38{\cdot}05 \times 10^{-3}$M. $Y_t$ = count per 100 min., corrected for background, on 5·98 c.c. of solution, after precipitation with 0·80 c.c. of 0·3079N-$AgNO_3$, filtration, and making the filtrate up to 10 c.c. with water. $k_1 = (2{\cdot}303/t)\log_{10}\{(\frac{1}{2}Y_\infty - Y_0)/(\frac{1}{2}Y_\infty - Y_t)\}$.

| $t$ (min.) | 0 | 19·3 | 32·5 | 61·8 | 110 | ∞ |
|---|---|---|---|---|---|---|
| $Y_t$ | 300 | 920 | 1310 | 2130 | 3400 | 7200 |
| $10^4k_1$ ($k_1$ in min.$^{-1}$) | — | 107 | 112 | 131 | 413 | — |
| % of 1 Cl exchanged | 8·3 | 25·5 | 36·2 | 59·0 | 94·0 | (200) |

(10*f*) *Kinetics by Potentiometric Titration of Chloride Ion.*—This form of analysis was used, for example, to follow displacement of chlorine by means of azide ion from the *cis*-dichlorobisethylenediaminecobalt(III) ion. One electrode was provided by a silver wire dipping in the solution, which was connected by a saturated potassium nitrate, agar-agar, salt-bridge to a calomel half-cell. The titrant was methyl-alcoholic silver nitrate, while the solvent of the

titrated solution was a mixture of 2 vols. of methyl alcohol and 3 vols. of acetone, to which was added a little nitric acid.

The reacting solutions were made up as usual under nitrogen and with exclusion of moisture, and reaction was allowed to proceed in a darkened thermostat. Measured samples were

*Table* 13. *Titrimetrically followed reaction of cis-*$[Co\,en_2Cl_2]^+Cl^-$ *with* $NaN_3$ *in* MeOH *at* 25·9. (*Run no.* 31.)

Initially $[\{Co\,en_2Cl_2\}^+Cl^-] = 0{\cdot}775 \times 10^{-3}$M, and $[NaN_3] = 1{\cdot}93 \times 10^{-3}$M. Titres are in c.c. of $1{\cdot}00 \times 10^{-3}$N-$AgNO_3$ for 10 c.c of reaction solution, and so the calculated initial titre is 7·75 c.c., while the calculated final titre for one chlorine atom replaced is 15·5 c.c. From the titre at the time of taking the first sample, $t = 0$, it follows that 16·14% of reaction has by then occurred. Therefore at $t = 0$, $[\{Co\,en_2Cl_2\}^+Cl^-] = 0{\cdot}650 \times 10^{-3} = a$ and $[NaN_3] = 1{\cdot}068 \times 10^{-3}$M $= b$. In terms of titres, $a = 6{\cdot}50$ c.c. and $b = 10{\cdot}68$ c.c. The rate constant is calculated from $k_2 = \{2{\cdot}303/t(b-a)\} \log_{10} \{a(b-x)/(b(a-x)\}$.

| $t$ (min.) | 0 | 8·25 | 22·5 | 62 | 87·5 | 139·5 | 171 | 207 | 261 | 321 | 446 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Titre (c.c.) | 9·0 | 9·45 | 9·8 | 11·05 | 11·6 | 12·55 | 12·90 | 13·35 | 13·85 | 14·1 | 14·65 |
| $x$ (c.c.) | 0 | 0·45 | 0·80 | 2·05 | 2·60 | 3·55 | 3·90 | 4·35 | 4·85 | 5·10 | 5·65 |
| $k_2$(min.$^{-1}$ mole$^{-1}$ l.) | — | 8·4 | 5·8 | 6·4 | 6·4 | 6·6 | 6·5 | 6·8 | 7·0 | 6·6 | 6·9 |
| % 1 Cl replaced | 16·1 | 21·9 | 26·4 | 42·6 | 49·6 | 62·0 | 66·5 | 72·3 | 78·7 | 82·0 | 89·0 |

Mean $k_2 = 6{\cdot}7$ min.$^{-1}$ mole$^{-1}$ l.

delivered into the acidified acetone at −80°, and, after the titration vessel had then been surrounded with ice-water, were titrated as rapidly as possible. A sample run is recorded in Table 13.

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## 548. *Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part III.* Steric Course of Some Unimolecular Substitutions in the* cis-*Dichlorobisethylenediaminecobalt*(III) *Ion.*

By D. D. BROWN and R. S. NYHOLM.

This is the first of a series of reports on the steric course of octahedral substitutions of *cis*- and *trans*-complexes of transition metals by mechanisms kinetically characterised. The present report is on unimolecular substitutions by chloride ion and by thiocyanate ion in the *cis*-cobalt(III) cation discussed in Part II.* It is shown that the optically inactive, quinquecovalent, heterolysis product, slowly formed in the common first stage of these unimolecular substitutions, takes up the substituting anion at comparable rapid rates in all the distinguishable positions among its retained ligands. Two possible stereochemical pictures are offered, and some attempt is made to assess their relative likelihood.

IN Part II it is shown that the nucleophilic replacement of one chlorine atom in the *cis*-dichlorobisethylenediaminecobalt(III) ion by any of the four substituting agents, nitrate, chloride, bromide, and thiocyanate ion, in solvent methyl alcohol, is rate-controlled by one common process, which is of first order with respect to the cation, but is independent of the substituting anion, and results in a complete loss of optical activity from the cation. The explanation offered is that these are all unimolecular substitutions, rate-governed by a heterolysis of the cation, which eliminates the displaced group, and leaves an optically inactive quinquecovalent cobaltium ion :

$$[Co\,en_2Cl_2]^+ \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} [Co\,en_2Cl]^{++} + Cl^- \xrightarrow[\text{fast}]{X^-} [Co\,en_2ClX]^+ \quad . \; . \; . \; . \; . \; . \quad (S_N1)$$

With this cobaltium ion (as, for temporary convenience, we may informally call it †) the substituting anion combines in the final and rapid step of the unimolecular mechanism.

* Part II, preceding paper.

† The analogy is with "carbonium," the name applied to what is left when a maximally covalent form of carbon, $CR_4$, loses one ligand R with its bonding electrons.

The stereochemical problem which this mechanism presents is that of where, among the ligands remaining in the cobaltium ion, does the substituting agent enter. In order to answer this, it is necessary to find out what stereoisomeric products are formed, and, if there is more than one, how fast each is formed. We have studied this question in two examples taken from the field opened by the work of Part II.

(1) *Steric Course of Substitution by Chloride Ion in the* cis-*Dichloro-cation.*

(1*a*) *Spectrophotometric Study of Stereoisomeric Changes in the Dichloro-cation.*—We saw in Part II that the rate of loss of optical activity from the *cis*-dichloro-cation, which is identical with the radiochemically measured rate of substitution of bound chlorine by attacking chloride ion, follows accurately a first-order law. No measurable solvolysis, even of a temporary kind, occurs, for no net liberation of chloride ion can be detected at any time during or after the polarimetrically or radiochemically measured change. Thus the dissolved substance remains of the same composition from the beginning of the change to the end.

It does, however, suffer stereochemical isomerisation, apart from the loss of optical activity, because the colour changes from violet to green. Green is the colour of the *trans*-dichloro-cation, and, indeed, the absorption spectrum of the solution, if measured some time after the polarimetrically or radiochemically measured change is over, is quantitatively identical with that of a freshly prepared solution of the right amount of a salt of the *trans*-cation.

Two things follow. First, thermodynamically, the *trans*-cation is so much more stable than the *cis*- under the experimental conditions, that, in equilibrium, we have an inappreciable proportion of the *cis*-cation; in other words, the *trans*-cation is formed very nearly irreversibly. Secondly, from a kinetic viewpoint, while many routes of reversible change may be open to, and may be utilised by, the *cis*-cation, one route at least is available which leads to (and in principle from) the *trans*-cation.

The equality of rate between chlorine exchange and rotation loss is consistent with only two routes of molecular isomeric change: either alone might be pursued, or both might be pursued concurrently. They are as follows:

(A) Every original *l*-*cis*-cation* which suffers the occurrence destroying its optical activity directly yields as its monosubstitution product the *trans*-cation.

(B) Of any large number of original *l*-*cis*-cations undergoing the process which destroys their optical activity, 50% directly yield as their monosubstitution products new *l*-*cis*-cations, while the other 50% directly give *d*-*cis*-cations.

The above kinetic conclusion amounts to the statement that process (A) is involved. No matter whether it is involved exclusively, or whether it is pursued concurrently with process (B), even, perhaps, with process (B) operating to a predominating extent, thermodynamics will still determine that the final product is the pure *trans*-cation.

Thus all that remains unknown about the stereochemical course of the substitution is the proportion in which process (B) accompanies process (A). And this we can determine by comparing the rate of production of the *trans*-cation with the rate of loss of optical activity from original *cis*-cation.

The rate of production of the *trans*-cation has been determined spectrophotometrically. The absorption spectra of the *cis*- and *trans*-cations, shown together in Fig. 1, make it obvious that in order to make this measurement one has only to follow the fall in optical density at wave-length λ 5400 Å. A special series of experiments, with freshly prepared solutions of mixtures of weighed *cis*- and *trans*-dichlorobisethylenediaminecobalt(III) chlorides in various ratios, confirmed that the optical density is a strictly linear function of percentage composition.

The formation of the *trans*-isomer, as measured photometrically, was found to follow an overall first-order rate law. In detail, the process was of first order with respect to the *cis*-cation and of zeroth order with respect to chloride ion. The latter point was clearly shown by the trivial kinetic effect of large excesses of added lithium chloride: even with

* For this use of *d*- and *l*-, see *J.*, 1953, 2674 (footnote).

50-fold excess the rate was increased only by a factor of 1·5, as illustrated in Table 1. This small rate change is closely similar to that observed in measurements of the loss of optical rotation, and is to be similarly interpreted as an ionic strength effect. But at any given ionic strength the rate of formation of the *trans*-cation is not as great as the rate of loss of optical activity from the *cis*-cation. For the temperature 35·8°, the former rate is 82 ± 2% of the latter, as also appears from Table 1. In view of the other rate and product relations of which we have to take account as explained above, the stereochemical conclusion is that, of 100 original *l-cis*-cations once substituted at 35·8°, 82 produce *trans*-cations, 9 give new *l-cis*-cations, and 9 yield *d-cis*-cations.

TABLE 1.—*Rate of conversion of cis-*$[Co\ en_2Cl_2]^+Cl^-$ *into trans-*$[Co\ en_2Cl_2]^+Cl^-$ *alone and in the presence of* LiCl *in anhydrous* MeOH *at* 35·8°.

| Run No. | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|
| $[\{Co\ en_2Cl\}^+Cl^-]$ (mmole/l.) | 1·75 | 1·92 | 2·12 | 1·79 | 1·76 |
| [LiCl] (mmole/l.) | — | 25·2 | 50·0 | 72·0 | 90·2 |
| $10^3\ \mu$ ($\mu$ = ionic strength) | 1·75 | 27·1 | 52·1 | 73·8 | 92·0 |
| $[Cl^-]/[\{Co\ en_2Cl_2\}^+]$ | 1·0 | 14·1 | 24·6 | 41·2 | 52·3 |
| $10^4k_1^{phot\text{-}Cl}$ (with $k_1$ in sec.$^{-1}$) | 0·88 | 1·07 | 1·12 | 1·20 | 1·30 |
| $10^4k_1^{pol\text{-}Cl}$ (from Part II) | 1·05 | 1·28 | 1·40 | 1·52 | 1·58 |
| $k_1^{phot\text{-}Cl}/k_1^{pol\text{-}Cl}$ | 0·84 | 0·84 | 0·80 | 0·79 | 0·82 |

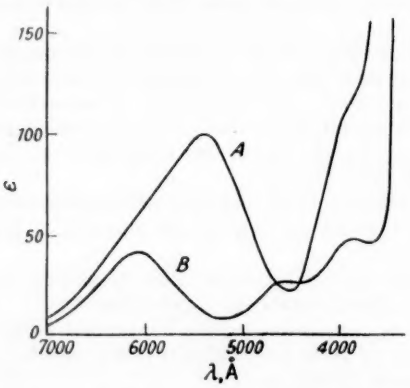


FIG. 1.
*Absorption spectra:*
*A* = *cis*-$[Co\ en_2Cl_2]^+Cl^-$.
*B* = *trans*-$[Co\ en_2Cl_2]^+Cl^-$.

The photometrically measured rate of production of the *trans*-isomer has a positive temperature coefficient, as shown by the data in Table 2. Formally, the results can be represented by an Arrhenius equation, with 23·69 kcal./mole as the activation energy, and $5·09 \times 10^{12}$ sec.$^{-1}$ as the frequency factor. The temperature coefficient of the rate of formation of the *trans*-cation is thus a little larger than that of the rate of rotation loss from the *cis*-cation, with the result that, as the temperature is raised, the former rate becomes a larger fraction of the latter, as also appears in Table 2.

TABLE 2.—*Temperature dependence of the rate of conversion of cis-*$[Co\ en_2Cl_2]^+Cl^-$ *into trans-*$[Co\ en_2Cl_2]^+Cl^-$ *in* MeOH.

| Run No. | 14 | 9 | 15 | 16 |
|---|---|---|---|---|
| $[\{Co\ en_2Cl_2\}^+Cl^-]$ (mmole/l.) | 1·77 | 1·75 | 2·06 | 1·92 |
| $T° - 273·16°$ | 26·31 | 35·84 | 45·43 | 53·83 |
| $10^4k_1^{phot\text{-}Cl}$ (with $k_1$ in sec.$^{-1}$) | 0·261 | 0·883 | 2·74 | 7·43 |
| $10^4k_1^{pol\text{-}Cl}$ (from Part II) | 0·313 | 1·05 | 3·07 | 7·95 |
| $k_1^{phot\text{-}Cl}/k_1^{pol\text{-}Cl}$ | 0·83 | 0·84 | 0·89 | 0·93 |

Of more significance than the temperature coefficient of the rate of formation of the *trans*-isomer, is the temperature coefficient of the ratio of the rates of formation, from original *cis*-cation, of *trans*-cation and of new *cis*-cation. For this should give directly the difference between the Arrhenius energies of activation of the alternative final fast steps of the

unimolecular mechanism, the recombination of chloride ion with the cobaltium ion in the stereochemically distinguished positions. If we label the steps of the mechanism (1), (2), and (3), as is done below, then we know from the record of Part II that the Arrhenius activation energy of the slow heterolysis (1) is $E_1 = 22{\cdot}64$ kcal./mole; and what we can try to find out is $E_2 = E_3$, the difference between the Arrhenius energies of activation of those final processes of ionic reunion that lead to the *trans*-cation (2), and to the enantiomeric *cis*-cations (3):

$$l\text{-}cis\text{-cation} \xrightarrow[\text{slow}]{(1)} \left\{\begin{array}{l}\text{cobaltium ion}\\ \\ +\ \text{chloride ion}\end{array}\right\} \begin{array}{l}\xrightarrow{(2)\ \text{fast}}\ trans\text{-cation}\\ \xrightarrow{(3)\ \text{fast}}\ (d+l)\text{-}cis\text{-cation}\end{array}$$

Qualitatively, it is obvious from the trend of the rate ratios given in Table 2 that $E_2 - E_3$ is positive, *i.e.*, that a larger energy barrier resists the entry of chloride ion into the cobaltium ion to form the *trans*- than to form the *cis*-dichloro-cation. For the purpose of quantitatively evaluating $E_2 - E_3$, our results are not as precise as could be wished; but we can make something of them by using the Arrhenius equation as a smoothing device, that is, calculating back, from the equations given in Part II and here, smoothed

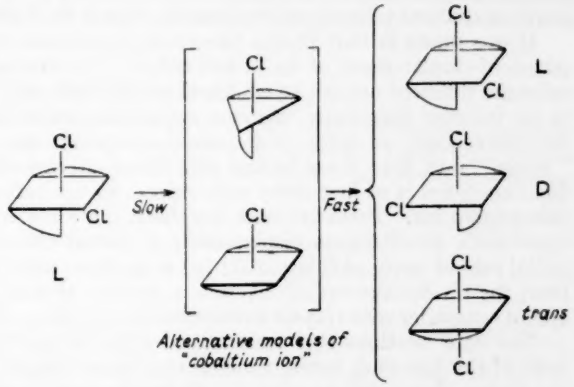


FIG. 2. *Schematic picture of* $S_N1$ *substitution.*

polarimetric and spectrophotometric rates, and thus smoothed ratios of the rates of production of *trans*-cation and of *dl-cis*-cation, for the four investigated temperatures. From these ratios, by an application of the Arrhenius equation, we find $E_2 - E_3 \approx 5$ kcal./mole.

(1*b*) *Stereochemial Picture of the Course of Unimolecular Substitution by Chloride Ion in the* cis-*Dichloro-cation.*—The relations described between the rate of chlorine exchange in this system, the rate of loss of optical activity, and the rate of appearance of the *trans*-isomer, show that the original *cis*-cation is first slowly heterolysed to give an optically inactive cobaltium ion, which then rapidly recombines with chloride ion in all the stereochemically possible ways. Two pictures can be given of this process, as is shown in Fig. 2. They differ with respect to the geometry of the quinquecovalent cobaltium ion, which can be based either on the model of the triangular bipyramid, or on that of the square pyramid: either would provide for the loss of optical activity. A final decision between these alternatives is not easy, but we offer an argument which seems to us to be a slight indication in favour of the triangular bipyramid.

In the triangular-bipyramid model of the cobaltium ion, the atoms are related nearly as they would be if the ion were formed by taking a chloride ion out of the *cis*-dichloro-cation without geometrical reorganisation. Therefore very little reorganisation is required when the bipyramidal ion combines with a chloride ion to give the *cis*-dichloro-cation. On the other hand, the bipyramidal ion can combine with chloride ion to produce the *trans*-dichloro-cation only with an accompanying displacement of one end of an ethylenediamine residue. Hence we should expect a higher energy barrier to oppose the union

of the bipyramidal ion with chloride ion to give the *trans*- than to give the *cis*-dichloro-cation: in terms of our previous notation, $E_2 - E_3$ should be positive.

In the square-pyramidal model of the cobaltium ion, the atoms are related just as they would be if the ion had been formed by removing a chloride ion from the *trans*-dichloro-cation without further geometrical change. Therefore no reorganisation is required when the square-pyramidal ion combines with chloride ion to produce the *trans*-dichloro-cation. On the other hand, the square-pyramidal ion can combine with chloride ion to give the *cis*-dichloro-cation only with displacement of one end of an ethylenediamine residue. Hence we should expect a higher energy barrier to resist union of the square-pyramidal ion with chloride ion to form the *cis*- than to form the *trans*-dichloro-cation: in symbols, $E_2 - E_3$ should be negative.

In the preceding Section the experimental result was given that $E_2 - E_3$ is positive. This favours the triangular-bipyramidal model of the cobaltium ion.

(2) *Steric Course of Substitution by Thiocyanate Ion in the* cis-*Dichloro-cation.*

(2*a*) *Spectroscopic Study of the Proportions of Formed Stereoisomeric Chlorothiocyanato-cations.*—This substitution was examined more briefly than the chloride-ion substitution, because the precision of the measurements proved to be lower, in particular, too low to justify a study of temperature coefficients such as that already described.

It was shown in Part II that the *cis*-dichloro-cation undergoes both of the two possible stages of displacement of its bound chlorine by entering thiocyanate ion, but that the rates are different enough to enable about the first 40% of the first stage of substitution to be followed kinetically, without appreciable interference from the second stage. If, for convenience, we speak of the observed specific rate of reaction in this range as the "initial" rate, then it can be said that the initial rate of entry of thiocyanate ion into the dichloro-cation is of first order with respect to the cation and zero order with respect to thiocyanate ion. Provided that the thiocyanate ion is in such excess as to exclude an appreciable simultaneous displacement of bound chlorine by entering chloride ion, the initial rate of entry of thiocyanate ion is identical with the rate of loss of optical activity from the *cis*-dichloro-cation, likewise a process of first order with respect to the cation and of zero order with respect to the substituting anion, whether chloride or thiocyanate ion.

The rate relations here summarised could be produced by substitution in either or both of the following forms, namely, that every original dichloro-cation which undergoes the change destroying its optical activity gives either the *trans*-chlorothiocyanato-cation, or the *d*- or *l*-*cis*-chlorothiocyanato-cation, as its first substitution product.

We have to consider the most general possibility, which is that these two types of molecular process occur concurrently; and we can ascertain the proportions in which they do so, if, having found, as in Part II, the total rate of entry of the first thiocyanato-substituent, we determine, for the same conditions, the rate of formation of, say, the *cis*-chlorothiocyanato-cation separately. How this may be done optically can be appreciated by glancing at Fig. 4 of Part II. The absorption curves of the *cis*-dichloro-cation and the *trans*-chlorothiocyanato-cation intersect at the wave-length 5000 Å; and hence, at this wave-length, the formation of the *trans*-substitution product leaves no optical record. At the same wave-length, the *cis*-chlorothiocyanato-cation has a much larger optical absorption than the original *cis*-dichloro-cation; and therefore an observation of the change of optical density at this wave-length will measure solely the formation of the *cis*-substitution product. The results of such measurements can be expressed by stating what proportion of the total chlorothiocyanato-cation, which has been formed at any time during the followed portion of the reaction, consists of the *cis*-isomeride. Mean values of this proportion, as measured over about the first 40% of monosubstitution, are given in Table 3. To within the somewhat large experimental error, they signify that of 100 original *l*-*cis*-dichloro-cations once substituted by thiocyanate ion at 35·8°, 36 produce *trans*-chlorothiocyanato-cations, while 64 give *cis*-chlorothiocyanato-cations.

(2*b*) *Stereochemical Picture of the Course of Unimolecular Substitution by Thiocyanate Ion in the* cis-*Dichloro-cation.*—The relations described among the various rates measured

for this substitution show that the *cis*-dichloro-cation is first slowly heterolysed to the already discussed cobaltium ion, which then rapidly combines with the thiocyanato-ion in all the stereochemically possible ways.

As we have not investigated the temperature dependence of the rate of this ionic union in its different stereochemical forms, we cannot with certainty interpret the observation that, in the conditions used, the thiocyanate ion goes mainly into *cis*-positions,

TABLE 3.—*Proportions of cis*-[Co $en_2Cl(NCS)]^+$ *in the total* [Co $en_2Cl(NCS)]^+$ *formed from cis*-[Co $en_2Cl_2]^+$ *by substitution with* $NCS^-$ *in* MeOH *at* 35·8°.

| Run No. | 23A | 25A | 26A | 27A |
|---|---|---|---|---|
| [{Co $en_2Cl_2$}$^+Cl^-$] (mmole/l.) | 0·72 | 0·67 | 0·67 | 0·59 |
| [LiNCS] (mmole/l.) | 13·7 | 30·0 | 49·7 | 90·0 |
| Percentage of *cis*-[Co $en_2Cl(NCS)]^+$ | 58 | 67 | 64 | 66 |

although chloride ion predominantly takes the *trans*-position. However, this difference seems to involve no general stereochemical principle. The small rate ratios which create the distinction could well arise from differences of interaction between the substituting agent and the bound chlorine atom in the cobaltium ion. If such effects led to a different activation-energy difference for *trans*- and *cis*-combination of the thiocyanate ion than of the chloride ion, then at other temperatures the thiocyanate ion would partition its attack qualitatively like the chloride ion.

### (3) *Illustrative Experimental Data.*

Materials were prepared for this work as outlined in Part II, where the spectrophotometric technique, as here employed, is described. No more is therefore necessary than to illustrate, as is done in Tables 4 and 5, the production of the results which have been summarised above

TABLE 4.—*Change of optical density at* 5400 Å *during isomerisation of cis*-[Co $en_2Cl_2]^+Cl^-$ *in the presence of* LiCl *in* MeOH *at* 35·8°. (*Run no.* 13.)

[{Co $en_2Cl_2$}$^+Cl^-$] = $1·763 \times 10^{-3}$M; [LiCl] = $90·2 \times 10^{-3}$M; $D$ = optical density in a 2-cm. cell for λ 5400 Å; $k_1 = (2·303/t) \log_{10} (D_\infty - D_0)/(D_\infty - D_t)$.

| $t$ (min.) | 0 | 29 | 62·5 | 89 | 119 | 151·5 | 180 | 210·5 | 220 | 239·5 |
|---|---|---|---|---|---|---|---|---|---|---|
| $D_t$ | 0·296 | 0·245 | 0·1975 | 0·168 | 0·138 | 0·1165 | 0·0975 | 0·0815 | 0·0795 | 0·074 |
| % Reaction | 0 | 20·9 | 38·3 | 49·4 | 60·6 | 68·4 | 75·5 | 81·4 | 82·1 | 84·4 |
| $10^4k_1$ (min.$^{-1}$) | — | 80 | 77 | 76 | 78 | 76 | 78 | 80 | 78 | 78 |

Directly observed $D_\infty$ = 0·032. Mean $k_1$ = 0·0078 min.$^{-1}$.

TABLE 5.—*Change of optical density at* 5000 Å *during substitution of cis*-[Co $en_2Cl_2]^+Cl^-$ *with* LiNCS *at* 35·8° *in* MeOH. (*Run no.* 25A.)

Initially [{Co $en_2Cl_2$}$^+Cl^-$] = $0·674 \times 10^{-3}$M; [LiNCS] = $30·0 \times 10^{-3}$M. $D$ = optical density in a 4-cm. cell for λ 5000 Å.

| $t$ (min.) | 0 | 21·5 | 29·7 | 43·0 | 53·7 | 66·0 | 79·3 |
|---|---|---|---|---|---|---|---|
| $D_t$ | 0·171 | 0·203 | 0·211 | 0·224 | 0·233 | 0·248 | 0·261 |
| % Reaction giving *cis*- | 0 | 9·4 | 11·7 | 15·6 | 18·2 | 22·6 | 26·4 |
| % Total reaction * | 0 | 13·8 | 17·0 | 23·7 | 27·4 | 34·1 | 40·6 |
| % *cis*- in product | — | 68·0 | 68·8 | 65·9 | 66·3 | 66·3 | 65·0 |

$D_\infty$ if total product were *cis*-, as calculated from absorption spectrum = 0·512.

* Determined (Run 25) as described in Part II.

for each of the reactions studied with respect to the stereochemical composition of the first substitution product.

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## 549. *Excited States of Acetylene. Part I. Possibilities of Interaction between σ-Bond Hybridisation and π-Electron Excitation with Resulting Changes of Shape during Transitions.*

By C. K. Ingold and G. W. King.

In π-electron excitations of unsaturated molecules, the lowest orbitals available to receive the promoted electron, supposing the σ-bond structure to remain unaltered, may interpenetrate so strongly with occupied σ-orbitals neighbouring the centre of unsaturation, that energetically lower promotions can be realised at the cost of a changed σ-bond hybridisation. The result is a gross change of shape on excitation, as is illustrated by a preliminary consideration of the case of acetylene. An unappreciated prevalence of such changes may be the reason why so few upper states of polyatomic molecules have as yet been characterised.

The study of lower excited states, and thus of potentialities for electronic deformation in normal states, of those molecules which are parent forms of the distinctive units of unsaturation in organic chemistry, should logically be taken in the order, ethylene, acetylene, benzene, to deal first with the range of cases in which the only unsaturated element is carbon. However, the reverse order of attack on these three molecules has been found the more practical, because it is the order of increasing difficulty, and thus better permits the necessary process of self-education.

Before the present, already briefly reported, study of acetylene (*Nature*, 1952, **169**, 1101), the only fully established assignment of a near-ultra-violet transition of any molecule of more than two atoms to a well-characterised upper electronic state was that of the $B_{2u}$–$A_{1g}$ transition of benzene. It happens that for benzene the excited ($B_{2u}$) state is of exactly the same shape and very nearly the same size as the normal ($A_{1g}$) state. Perhaps this has been a historical disadvantage: for one of the reasons why only one electronic band-system of a polyatomic molecule has yet been successfully analysed—only one upper state characterised—may be that analysis has too often been attempted under the preconception that the upper state would be something like the lower in form: the Franck–Condon principle has been interpreted as implying that major changes of shape on excitation are unlikely. On the other hand, Mulliken suggested that an upper state of a simple molecule may differ in form from the lower, when he pointed out that the near-ultra-violet band-system of carbon disulphide is too complicated to represent a transition from a linear ground state to a linear upper state. He worked out the band-structures that could result from the excitation of a linear triatomic molecule to a bent upper state; but the actual upper state involved in the carbon disulphide transition was not elucidated (*Phys. Review*, 1941, **59**, 873; **60**, 506).

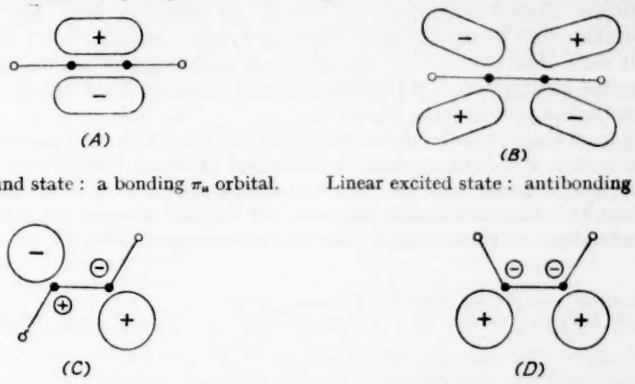
The need for keeping in view the possibility of a gross change of form, essentially a change of σ-orbital hybridisation, when one is attacking the analysis of a near-ultra-violet band-system of a π-electron molecule such as acetylene, is indicated by the following elementary considerations—these impressed themselves on us during our study of data herewith presented, but (as one of us discovered in a conversation in Dunedin in August 1952) were independently evolved in purely theoretical work by Dr. F. A. Johnson, who up to that moment had known nothing of this investigation.

The normal acetylene molecule is linear ($D_{\infty h}$ in the notation of symmetry theory), and its highest occupied orbitals are those of the unsaturation shell, that is, the two equivalent bonding orbitals $\pi_u$, one of which is schematically represented in Fig. 1 at (*A*). Supposing that the molecule retains its linear shape on excitation, the lowest unoccupied orbital into which an electron from a $\pi_u$ orbital could be lifted is that obtained by introducing a central nodal surface normal to the internuclear line, the antibonding $\pi_g$ orbital, represented in Fig. 1 at (*B*). There must be much steric repulsion between any electron occupying this orbital and the electrons of the C–H bonds. An even worse position would arise, if we should try to promote a $\pi_u$ electron to the antibonding $\sigma_u$ orbital, which

also has a nodal plane across the middle of the molecule, but is concentrated about the molecular axis, mainly outside the C–C span, with the result that an occupying electron would be very strongly interpenetrated with the C–H-bond electrons. Faced with these more or less difficult alternatives, the molecule might well find it more energetically economical so to alter its σ-bond hybridisation that orbitals for the reception of the excited electron are made available which lie considerably further out of the way of the C–H bonds.

It is clearly possible that the linear ($sp$) hybridisation, which determines the σ-bond framework of the normal acetylene molecule, might change in the direction of plane-trigonal ($sp^2$) hybridisation, so that bond angles become reduced from 180° towards 120°. The simplest form which such an occurrence could take is that in which the change of hybridisation $sp \longrightarrow sp^2$ is complete, so that the excited acetylene molecule assumes the shape of a normal ethylene molecule from which two hydrogen atoms have been removed: they might be two *trans*- or two *cis*-related hydrogen atoms. In place of each removed hydrogen atom we shall have, in first approximation, a plane-trigonal atomic orbital capable of holding up to two unshared electrons. This is schematically represented

FIG. 1. *Schematic representation of orbitals which may lose or gain an electron in transitions between the normal molecule of acetylene and various possible models of the excited molecule.*




Linear ground state: a bonding $\pi_u$ orbital.

Linear excited state: antibonding $\pi_g$ orbital.

*trans*-Bent excited state: $sp^2$ atomic orbitals constituting nearly non-bonding molecular orbitals.

*cis*-Bent excited state: $sp^2$ atomic orbitals constituting nearly non-bonding molecular orbitals.

in Fig. 1 at (*C*) and (*D*), the diagrams illustrating what we may call the *trans*- and *cis*-bent molecules of excited acetylene (in symmetry notation, the $C_{2h}$ and $C_{2v}$ models respectively).

For either model, in this first approximation, the two $sp^2$ atomic orbitals are collectively equivalent to two non-bonding molecular orbitals of identical energy: those of the $C_{2h}$ model will be labelled $a_g$ and $b_u$, and those of the $C_{2v}$ model $a_1$ and $b_1$. The energies of these non-bonding orbitals are expected to lie between that of the bonding $\pi_u$ orbital and that of the antibonding $\pi_g$ orbital of the linear molecule. Thus, provided that the σ-bonding is not too much weakened by the hybridisation change, the production of these $a$ and $b$ orbitals of bent states should allow an excitation of lower energy than would the $\pi_g$ orbital of the normal state of acetylene.

In closer approximation, the $sp^2$ atomic orbitals must be expected to interact slightly, so that electrons entering them will not be wholly unshared, and the generated molecular orbitals will neither be completely non-bonding nor accurately degenerate. In the $C_{2h}$ model, the orbital we label $b_u$ will be slightly bonding, and the orbital $a_g$ slightly anti-bonding. In the $C_{2v}$ model, orbital $a_1$ will be weakly bonding and $b_1$ weakly antibonding.

Such refinements will concern us later; but for the present the broad energetic distinction between the approximately non-bonding orbitals of the bent models, and the strongly bonding and anti-bonding orbitals of the linear model, will justify taking bent states into account as possibilities, when attacking the analysis of near-ultra-violet band-systems of triple-bonded molecules such as acetylene. In our problem we shall take them

into account in the broadest way, without preconception as to the quantitative magnitude of any hybridisation change, which has, indeed, to be determined by the analysis. Our subsequent references to the *trans*- and *cis*-bent (or $C_{2h}$ and $C_{2v}$) models will imply nothing about bond angles, except that they are equal * and less than 180°.

The above discussion restricts attention to planar models of excited acetylene. One can, of course, imagine also three-dimensional models of the excited molecule, *e.g.*, models of symmetry $C_2$, in which the two bond angles lie in different planes, much as in the usually considered model of the normal state of hydrogen peroxide. However, elementary structural theory does not suggest that models of this character would be represented among the lower excited states of acetylene; and it is only with the lowest excited state that we shall be concerned. In order to produce the above planar models, one $\pi$ orbital of the normal molecule has to be destroyed: to make a three-dimensional model both $\pi$ orbitals must become disrupted. Moreover, the hybridisation change needed to produce the three-dimensional molecule must be more drastic than from $sp$ to $sp^2$; it would have to extend towards $sp^3$ at least, if not towards $p$. A preliminary recognition of the improbability of finding a three-dimensional state among the lowest excited states of acetylene is useful, because we have to develop the theory of electronic transitions between models of different shapes sufficiently to provide an adequate basis for the analytical problem undertaken, but, because of the complicated nature of such theory, we do not want to generalise it more than necessary. Therefore, we have approached our problem on the basis of the limited assumption that the relevant excited state, if not linear, will at least be planar: this optimism proved to be justified.

Proceeding from these considerations, we shall next deal with the experimental and the theoretical tools used, and then we shall describe and interpret the first ultra-violet band-system of acetylene, drawing conclusions about the geometrical and dynamical characteristics, and about the electronic constitution, of the excited state of the molecule. For a preliminary indication of these conclusions the Summary of Part IV (p. 2725) may be consulted.

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## 550. *Excited States of Acetylene. Part II.*† *Experimental Methods of Recording the Near-ultra-violet Absorption Spectra of Acetylenes.*

By C. K. Ingold and G. W. King.

The ultra-violet absorption spectra of acetylene and dideuteroacetylene between 2500 and 2100 Å have been studied, attention being paid, not only to the coarse structures of the spectra, and the fine structures of the bands of the acetylene spectrum, but also to the Boltzmann variation, and to the Franck–Condon distribution of band intensity. The methods used are outlined.

Two isotopic modifications of acetylene, $C_2H_2$ and $C_2D_2$, have been studied. The $C_2H_2$, drawn from a cylinder or made from calcium carbide, was purified by means of reagents, condensed, and sublimed. The $C_2D_2$, made by interaction of $D_2O$ with calcium carbide of special quality, kindly supplied by British Industrial Solvents, Limited, through the courtesy of Mr. W. P. Phillips, was condensed and purified by fractional sublimation. Its degree of isotopic purity was checked by spectroscopic and by mass-spectrographic analysis.

The spectra of these acetylenes were recorded in absorption between 2500 and 2100 Å, and it was necessary to obtain as much resolving power as possible from the available

* Equality of angles follows from the highly plausible assumption that, in any $\pi$ excited state, the two CH groups remain equivalent.

† Part I, preceding paper.

quartz-prism equipment. As heretofore, the microphotometer was used as an aid to frequency measurements. Temperatures from −80° to +200° C were used, absorption paths from 0·03 to 20 metre-atmospheres, and exposures from a few minutes to several days. The intensities of the more important bands were measured. All these branches of the observational work proved important for the eventual analysis of the spectra.

## Experimental

*Preparative Methods.*—(a) *Acetylene.* The gas from a cylinder, after being passed through traps cooled in solid carbon dioxide, was condensed in a receiver cooled in liquid nitrogen, and resublimed through a $CO_2$-cooled trap. Alternatively, acetylene, generated from calcium carbide, was passed through a purifying train, and condensed and resublimed as before. The spectrally pure gas from either source was stored in large glass bulbs, and when required was frozen out, and subsequently distilled into the evacuated absorption cell.

(b) *Dideuteroacetylene.* The special carbide (*ca.* 10 g.) was baked out with continuous pumping at 400° for 2 hr. in the all-glass generating apparatus, and, after admission of dry nitrogen, 99·6% deuterium oxide (2—3 g.) was allowed slowly to drip on to the carbide, which was meanwhile cooled with an external bath of solid carbon dioxide and alcohol, or was allowed to warm slightly, as needed to regulate the reaction. The generated gas passed through a $CO_2$-cooled trap and was condensed in a receiver cooled in liquid nitrogen. After evacuation of the receiver, the heavy acetylene was resublimed several times through $CO_2$-cooled traps into $N_2$-cooled receivers with rejection of head and tail fractions.

(c) *Isotopic analysis.* Preparations of heavy acetylene were at first qualitatively checked for isotopic composition by two spectral methods. A discharge at 1000 v and 50 cycles was passed through the gas at 5 mm. in a small discharge tube; no trace of the bands of the CH molecule at 4315 and 3872 Å could be found, although the band of CD at 4307 Å was easily observed. The infra-red spectrum of the gas at 70 cm. pressure in a 4-cm. cell was recorded in the region 2—4$\mu$: the band of $C_2H_2$ at 3282 cm.$^{-1}$ did not appear, but the band of $C_2HD$ at 3335 cm. was present, though it was very weak compared with the band of $C_2D_2$ near 2439 cm.$^{-1}$.

A quantitative analysis was made, with Dr. C. A. Bunton's kind co-operation, by means of the mass-spectrometer. The heavy acetylene itself could not be introduced into the ion-source, because it attacked the hot filament. It was therefore decomposed to carbon and heavy hydrogen, and the latter was fed into the instrument. A coil of fine iron wire was first heated electrically in air so that it became oxidised on the surface, and was then heated in hydrogen until it was reduced. Its container was then exhausted, and subsequently filled with the heavy acetylene, and the wire was heated until just visible in the dark. Polymerisation of the acetylene did not occur, but long strands of carbon were formed on the wire, and after a short time the change of pressure on freezing out of the residual acetylene showed that most of it had decomposed to give heavy hydrogen. Analysis of this in the mass spectrometer showed the presence of 2·5% of protium. We could not find any bands of acetylene in the ultra-violet spectrum of the dideuteroacetylene, but some of the weak unidentified bands in that spectrum may have belonged to the monodeuterated compound.

*Spectrographic Methods.*—(a) *The optical system.* The spectrograph was Hilger's automatically focusing, quartz-prism instrument E492 of Littrow pattern, with aperture *f*/30, and dispersion at the plate 42 cm.$^{-1}$/mm. at 2500 Å and 27 cm.$^{-1}$/mm. at 2000 Å. The slit was used with width 0·02 mm. Reduction below this figure did not increase the resolving power, which was about 40,000.

The other parts of the system were mounted, if possible, on the optical bench belonging to the spectrograph. Three absorption cells were used. Most of the stronger bands were photographed with a fused-quartz cell 55 cm. long, containing the gas at pressures from 5 cm. up to more than 1 atm. Light from the source passed through a quartz lens, which focused it through the cell directly on to the slit, the lens and cell windows subtending angles greater than the aperture *f*/30. For weaker bands, a cell 225 cm. long and of 2 cm. internal diameter was used, in conjunction with a mirror, so that its length was employed twice. In this way, with gas pressures up to 1·5 atm. absorption paths of up to 7 metre-atmospheres could be obtained. In order to fill the aperture of the spectrograph from such a long and narrow cell, it was necessary to bring the light to a focus within it at each transit. With this object the light source was placed near the slit, but to one side, and the light was reflected by a prism away from the spectrograph, through a quartz lens, and then through its first focus within the cell, and, beyond the other end, to a concave aluminised mirror, of 160 cm. radius, which returned it, through its

second focus within the cell, to the same quartz lens, which brought it to its third focus on the slit. For still weaker bands, a multiple reflexion cell of White's design (*J. Opt. Soc. Amer.*, **1942**, **32**, 285) was employed, which had been built in accordance with Bernstein and Herzberg's description (*J. Chem. Phys.*, **1948**, **16**, 30), by Dr. W. C. Price, who very kindly lent it to us. The light emerging from this cell converged over a sufficient angle to fill the aperture of the spectrograph. With gas at just above atmospheric pressure, this cell gave an absorption path of 20 metre-atmospheres.

With continued use, the 55- and 225-cm. cells became opaque to light of shorter wave-length than about 2300 Å: the transparency of the windows was periodically restored by heating them to about 600°. The multiple reflexion cell was not transparent to wave-lengths shorter than 2300 Å; but we wanted it only for the long-wave end, which is the weak end, of the acetylene spectrum. Whilst all three cells were used for ordinary acetylene, only the 55- and the 225-cm. cell were employed for dideuteroacetylene, because it required 30 l. of gas to fill the multiple reflexion cell, and our stock was not sufficient for the purpose.

In order to permit study of the effect of temperature on band intensities, arrangements were made to cool and to heat the 55- and the 225-cm. cell. The temperatures used ranged from −78° to +200°. When the effect of reduced temperatures on the intensities of the strongest bands was studied, with use, necessarily, of low gas-pressures, and of the short cell with cooled sides and windows warmed to stop frosting, results were at first obtained which indicated that the gas was not coming even approximately into thermal equilibrium with the cooled cell-walls. This difficulty was overcome by making up the total pressure to 1 atm. with added hydrogen. It was shown that the addition of hydrogen did not alter band intensities when the walls, windows, and surrondings of the cell were at a uniform raised temperature.

The light source was a small hydrogen discharge lamp in a quartz envelope. Calibration spectra from a Pfund-type iron arc were placed immediately above and below the absorption spectrum.

(b) *Photography.* The spectral region 2400—2100 Å was photographed on Ilford Q 1 plates, which have the optical characteristics of Schumann plates, though their sensitive films are much more robust: they have very little gelatin, the photographic salts being in and on its surface. The plates are fine grained, and were found not to reduce the obtainable resolving power. However, they show but little contrast; and so, in order to obtain satisfactory records of, for example, the head and tail of a band, it was often necessary to make several exposures with different gas pressures. The region 2500—2400 Å was photographed on Kodak L15 plates, which have a normal type of bromide emulsion.

With absorption paths ranging from 0·03 up to 20 metre-atmospheres, exposure times ranged from some minutes to several days, and control of temperatures was therefore necessary. All the apparatus so far mentioned was contained in a room which had thermostatic regulation, and was kept throughout this work at 20·0° ± 0·1°.

(c) *Microphotometry.* Final measurements of frequency, and measurements of intensity, were made from records obtained from the spectrograms with the aid of a Zeiss recording microphotometer. The width of its monitoring slit was adjusted to give the best resolution consistent with a minimum of background due to graininess. The optimal width was that which selected 0·03 mm. of the spectrogram, a spectral interval of about 1 cm.$^{-1}$. The ratio arm of the microphotometer was so adjusted that the dispersion on the record was about 2 cm.$^{-1}$/mm.

After a section of the acetylene spectrum had been recorded, then, without any settings being altered except that of a diaphragm adjacent to the slit, and, of course, without plate or record holder being touched, the monitoring light was made to traverse, in the same direction, the corresponding section of the iron-arc calibration spectrum, the traces of the two spectra being thus imprinted on the same record.

(d) *Measurement of frequency.* Each microphotometer record was measured on a two-way travelling microscope accurate to 0·01 mm.

The measured maxima consisted of all the acetylene peaks, together with many iron-arc lines for calibration, chosen with preference for those whose wave-lengths have been determined interferometrically by Meggers. The wave-lengths were taken from Harrison's list "M.I.T. Wave-length Tables," and converted to frequencies in vacuum with the aid of Kayser's "Tabelle der Schwingungszahlen."

The interpolated acetylene frequencies, each based on records obtained from three independent primary spectrograms, were computed to 0·01 cm.$^{-1}$, and recorded as means rounded to 0·1 cm.$^{-1}$, the general consistency being about 0·2—0·3 cm.$^{-1}$. Lines separated by less than about 1·2 cm.$^{-1}$ appeared as a single diffuse line; but its diffuseness, disclosing a composite

nature, could be seen; and this was still true for separations down to 0·5 cm.$^{-1}$, as subsequently determined by calculation, after the spectrum had been analysed. Much of the fine structure of the acetylene spectrum was resolved, but not much of that of the dideuteroacetylene spectrum, where there is more overlapping of bands, and the rotational structure is more closely spaced.

(e) *Measurement of intensity.* Intensities were measured of a number of bands of the strongest progression in the spectrum of acetylene. The essential measurement is that of the optical density, $D_L$, as a function of the frequency $\nu$ over the frequency range covered by the band. The optical density is defined by $D_L = \log_{10}(I_0/I_L)$, where $I_0$ and $I_L$ are light intensities at a definite frequency, through the cell empty, and filled to a pressure expressed by the absorption path $L$. From the measurements of $D_L$, it is necessary to obtain by quadrature, the quantity $\int D_L d\nu$ over the band, $\nu$ being expressed in cm.$^{-1}$.

A disc sector with variable aperture, calibrated in terms of optical density, and put immediately in front of the light source, was run at 3000 interruptions per minute. The slit width was kept as usual at 0·02 mm. Preliminary experiments in which the speed was varied by factors of two gave unaltered values of $D_L$, and others with the slit opened to 0·08 mm. gave unchanged values of $\int D_L d\nu$. Exposure times were standardised to 15 min. Extremes of image density were avoided.

Ilford Q1 plates were employed. The absorption tube being evacuated, the plate was first calibrated for optical density by making adjacent exposures with the sector aperture at $D = 0{\cdot}0, 0{\cdot}1, 0{\cdot}2, \ldots 1{\cdot}2$. The aperture was then opened to $D = 0{\cdot}0$, and a number of exposures were made with acetylene in the cell at various known pressures.

Microphotometer records were then made as follows. First, one of the acetylene bands was traced. Then, over the diagram of this trace, each calibration spectrum was traced. The effect of this was to divide the area under the contour of the band into a series of nearly horizontal slices of thickness equivalent to an optical density of 0·1. Also, the current to the lamp which illuminated the recording fibre of the microphotometer was momentarily interrupted by a cam-switch at regular intervals, to produce a series of vertical white lines 1 mm. apart on the record, which was thus divided into small rectangles. The band has a certain finite background density, which is taken as given by the lowest level densities flanking the band. The area, as found by counting rectangles, between the contour of the band and the background level, when multiplied by the dispersion, as obtained from the distances between acetylene maxima of known frequency, gives the quantity $\int D_L d\nu$.

The actual intensity of the band is, of course, independent of the absorption path $L$, and may be expressed by $\int \alpha d\nu$, where $\alpha$ is the absorption coefficient. In order to obtain the intensity thus expressed, the density integral $\int D_L d\nu$ had to be multiplied by $2{\cdot}303/L$, the absorption path $L$ being given by $273 L_0 p/T$, where $L_0$ is the length of the cell in cm., $p$ is the pressure of the gas in atmospheres, and $T$ is the absolute temperature. Values of $\int \alpha d\nu$ thus derived for the same band from several different spectrograms, for which $p$, and therefore $L$, had different values, were usually consistent to about $\pm$ 15%. The units of $\int \alpha d\nu$ are cm.$^{-2}$, and the mean values obtained for the bands measured are re-expressed in Part IV in dimensionless form as oscillator strengths. This involves multiplying $\int \alpha d\nu$ by a composite constant, which, as is shown in Part III, has in our cases the value $4{\cdot}78 \times 10^{-9}$ cm.$^2$.

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## 551. *Excited States of Acetylene. Part III.* Theoretical Methods for Analysis of Near-ultra-violet Band-systems of Acetylenes.*

By C. K. Ingold and G. W. King.

Rules of selection and intensity are developed in a sufficiently general form to permit discussion of coarse and fine structures, and also of intensity relations, in transitions of normal acetylene to non-linear but planar excited states.

### (1) Conventions and approximations

(a) *Co-ordinate Axes.*—In order to specify the motion of, and within, a polyatomic molecule, apart from its translatory motion, with which we shall have no concern, we need two sets of Cartesian axes, an " external " set, $X$, $Y$, $Z$, which may be taken as having its origin at the centre of mass of the molecule, but must have its axial directions fixed in space, and an " internal " set, $x$, $y$, $z$, which also may be given an origin at the centre of mass but must have its axial directions fixed in the molecule. Three Eulerian angles will describe the instantaneous orientation of the internal set relatively to the external set, and, in the wave function of the molecule, will be independent variables of special significance for rotation, and for the directional behaviour in space of the total angular momentum. Co-ordinates taken relatively to the internal axes, or linear combinations of such co-ordinates, will specify instantaneous electron positions, and the nuclear displacements; and, in the wave function, such co-ordinates will enter as independent variables important for the description of the relative movements of the electrons and nuclei, and of the directional distribution of angular momentum, whether due to rotation of the molecule, or to relative movements of its constituent particles, or to the spins of the latter.

It is convenient to take the internal axes, $x$, $y$, $z$, as coincident with the principal axes of inertia, $a$, $b$, $c$, traditionally so labelled that the corresponding principal moments of inertia stand in the order $I_a \leqslant I_b \leqslant I_c$. By deciding to maintain the same one-to-one correlation between $x$, $y$, $z$ and $a$, $b$, $c$, for the three models of acetylene that we shall be discussing, we can simplify notation by dropping the former labels, and employing the latter indiscriminately for internal co-ordinate axes and for the coincident axes of inertia. Indeed we shall use the same labels for axes of a third kind, *viz.*, axes of symmetry, since these, in so far as they are present at all, always coincide with axes of inertia, and therefore with our chosen internal co-ordinate axes. For the three acetylene models with which we shall be dealing, the internal axes are taken as indicated in Fig. 2.

The $D_{\infty h}$ model is a prolate symmetric top: two of its principal moments of inertia are equal, while the unique one is the smallest of the three, and, indeed, would be zero but for zero-point energy, and the finite mass of the electrons: $I_a \lll I_b = I_c$. The $C_{2h}$ and $C_{2v}$ models are asymmetric tops, but can be described as prolate near-symmetric tops: $I_a \ll I_b < I_c$. This arises from the considerably smaller mass of hydrogen than of carbon nuclei, taking into account also that, for such planar models, the relation $I_a + I_b = I_c$ will hold, apart from small deviations due to zero-point energy and electronic mass.

In the $D_{\infty h}$ model, $a$ is an infinity-fold axis, and perpendicular axes are two-fold axes of symmetry. In the other models, $a$ is not a symmetry axis, but in the $C_{2h}$ model $c$, and in the $C_{2v}$ model $b$, are two-fold axes. These symmetry properties are indicated in Fig. 2 by the symbols in brackets.

(b) *Approximate Factorisation of Wave Functions.*—It is a familiar idea that, in most circumstances, electronic orbital motion, nuclear vibration, and molecular rotation are nearly independent forms of motion, and that therefore, as an approximation, a wave-function $\psi$, which for energy $E$ satisfies the wave equation of the molecule

$$H\psi = E\psi$$

can be represented as the product of electronic, vibrational, and rotational factors satisfying the separate wave equations,

$$H_e\psi_e = E_e\psi_e \quad H_v\psi_v = E_v\psi_v \quad H_r\psi_r = E_r\psi_r$$

* Part II, preceding paper.

in the construction of which the original energy-operator and energy are treated as sums, and split into their component terms :

$$\psi = \psi_e\psi_v\psi_r \quad H = H_e + H_v + H_r \quad E = E_e + E_v + E_r \quad . \quad . \quad . \quad (1)$$

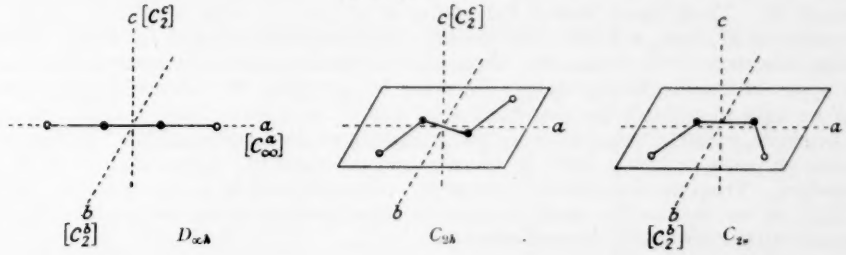
In discussing the symmetry properties of $\psi$ and its factors, it is often convenient, following Mulliken, to group the first two factors together, calling their product the " vibronic " wave function $\psi_{ev}$, whose energy $E_{ev}$ includes electronic and vibrational but not rotational energy

$$\psi_{ev} = \psi_e\psi_v \quad E_{ev} = E_e + E_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\psi \quad = \psi_{ev}\psi_r \quad E \quad = E_{ev} + E_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In this, as in any approximation, a complete representation of $\psi$ should contain an electronic spin factor $\psi_{es}$, and a nuclear spin factor $\psi_{ns}$; but we shall not show either explicitly. As to $\psi_{es}$, we assume that Pauli's principle is satisfied, so that $\psi_e\psi_{es}$ is anti-symmetric in the electrons; and we shall avoid discussing multiplicity by confining

FIG. 2. *Internal co-ordinate axes, principal axes of inertia, and axes of symmetry of the three models of acetylene.*




attention throughout to singlet electronic states, with the result that electron spin will not contribute to the total angular momentum represented in the quantum number $J$ of rotational states and energy levels. Accordingly, we shall simplify rotation by omitting the spin-multiplicity symbol throughout. As to $\psi_{ns}$, we note that its effect on hyper-multiplicity and thus on the statistical weights of energy levels, and on the intensities of individual transitions, is standard and independent of the special features of the present problem, so that we can introduce it when necessary without having to carry its theory in our formulæ.

## (2) Electronic States and Transitions

(a) *Classification of, and Selection Rules for, Electronic Wave Functions.*—Although we shall not have to discuss the explicit forms of $\psi$ and its approximate factors, we shall have to make repeated use of their symmetry properties, most, though not all, of which differ according to the molecular model of acetylene taken. Discussion of the factors of $\psi$ will lead to many selection rules, which are, however, approximate, because the factorisation is approximate. Discussion of $\psi$ itself will yield a small number of exact selection rules. We deal now with the electronic factor $\psi_e$, using the internal system of axes, $a$, $b$, $c$, with respect to which the symmetry properties of the different models differ.

First, as to the linear, or $D_{\infty h}$ model, the possible types of behaviour of the electronic wave function, under the operations to which the electronic wave equation is invariant, are as shown in Table 1, a multiple-purpose table, of which we need now notice only the left and the middle section. The latter contains the factors (" characters ") which multiply the different species of wave function, as a result of the operations, $2C_\phi^a$, $C_2^{bc}$, and $i$, of rotation by any angle $\pm\phi$ around $a$, of rotation by $\pi$ around $b$ or $c$, and of inversion through the origin; and also in consequence of the operation, $iC_2^{bc}$, of reflexion across any plane through $a$. The first column of the Table shows the labels of the symmetry species, chosen to correspond to those of diatomic molecules. The four species $\Sigma$ are non-

degenerate, and devoid of electronic angular momentum about the molecular axis $a$ ($\Lambda = 0$): the subscripts $g$ and $u$ mean symmetry and antisymmetry under operation $i$, while the superscripts + and − signify symmetry and antisymmetry for operation $iC_2^{bc}$. The infinitude of remaining species, $\Pi$, $\Delta$, etc., are each doubly degenerate, and have 1, 2, etc., units $h/2\pi$ of electronic angular momentum about the axis $a$ ($\Lambda = 1, 2$, etc.): $g$ and $u$ mean the same as before.

TABLE 1. *Species of electronic and vibrational wave functions of model* $D_{\infty h}$.

| Elec. | $\Lambda$ | $M$ | $E$ | $2C_\phi^a$ | $C_2^{bc}$ | $i$ | $2iC_\phi^a$ | $iC_2^{bc}$ | Vibs. | No. | $l$ | $T, R$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Sigma_g^+$ | 0 | — | 1 | 1 | 1 | 1 | 1 | 1 | $\Sigma_g^+$ | 2 | 0 | — |
| $\Sigma_u^-$ | 0 | — | 1 | 1 | 1 | −1 | −1 | −1 | $\Sigma_u^-$ | 0 | 0 | — |
| $\Sigma_g^-$ | 0 | — | 1 | 1 | −1 | 1 | 1 | −1 | $\Sigma_g^-$ | 0 | 0 | $(R_a)$ |
| $\Sigma_u^+$ | 0 | $M_a$ | 1 | 1 | −1 | −1 | −1 | 1 | $\Sigma_u^+$ | 1 | 0 | $T_a$ |
| $\Pi_g$ | 1 | — | 1 | $2\cos\phi$ | 0 | 2 | $2\cos\phi$ | 0 | $\Pi_g$ | 1 | 1 | $R_{bc}$ |
| $\Pi_u$ | 1 | $M_{bc}$ | 1 | $2\cos\phi$ | 0 | −2 | $-2\cos\phi$ | 0 | $\Pi_u$ | 1 | 1 | $T_{bc}$ |
| $\Delta_g$ | 2 | — | 1 | $2\cos 2\phi$ | 0 | 2 | $2\cos 2\phi$ | 0 | $\Delta_g$ | 0 | 2 | — |
| $\Delta_u$ | 2 | — | 1 | $2\cos 2\phi$ | 0 | −2 | $-2\cos 2\phi$ | 0 | $\Delta_u$ | 0 | 2 | — |
| ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |

The third column of Table 1 indicates the symmetry properties of the electric moment $M$. Their significance is that, when $\psi''\psi'$ contains a term with the symmetry properties of $M$, then, and then only, the intensity-controlling integral $\int\psi''M\psi'd\sigma$ will not vanish on account of the symmetry. Here the double prime marks the lower and the single the upper of the combining states. In order to determine the symmetry properties of $\psi''\psi'$ we have to multiply the characters of $\psi''$ and $\psi'$, as given in Table 1, and then, using the products, re-read Table 1 to obtain the symmetry of the species of $\psi''\psi'$. This is one of several purposes requiring Table 2, which shows the results (" direct products ") of this procedure. From the occurrences there of $\Sigma_u^+$ (the species of $M_a$), and of $\Pi_u$ (the species of $M_{bc}$), we can deduce the selection rules for transitions involving electronic oscillations parallel and perpendicular, respectively, to $a$.

TABLE 2. *Direct products of species of the model* $D_{\infty h}$.

| | $\Sigma_g^+$ | $\Sigma_g^-$ | $\Sigma_u^+$ | $\Sigma_u^-$ | $\Pi_g$ | $\Pi_u$ | $\Delta_g$ | $\Delta_u$ |
|---|---|---|---|---|---|---|---|---|
| $\Sigma_g^+$ | $\Sigma_g^+$ | $\Sigma_g^-$ | $\Sigma_u^+$ | $\Sigma_u^-$ | $\Pi_g$ | $\Pi_u$ | $\Delta_g$ | $\Delta_u$ |
| $\Sigma_g^-$ | | $\Sigma_g^+$ | $\Sigma_u^-$ | $\Sigma_u^+$ | $\Pi_g$ | $\Pi_u$ | $\Delta_g$ | $\Delta_u$ |
| $\Sigma_u^+$ | | | $\Sigma_g^+$ | $\Sigma_g^-$ | $\Pi_u$ | $\Pi_g$ | $\Delta_u$ | $\Delta_g$ |
| $\Sigma_u^-$ | | | | $\Sigma_g^+$ | $\Pi_u$ | $\Pi_g$ | $\Delta_u$ | $\Delta_g$ |
| $\Pi_g$ | | | | | $\Sigma_g^+\Sigma_g^-\Delta_g$ | $\Sigma_u^+\Sigma_u^-\Delta_u$ | $\Pi_g\Phi_g$ | $\Pi_u\Phi_u$ |
| $\Pi_u$ | | | | | | $\Sigma_g^+\Sigma_g^-\Delta_g$ | $\Pi_u\Phi_u$ | $\Pi_g\Phi_g$ |
| $\Delta_g$ | | | | | | | $\Sigma_g^+\Sigma_g^-\Gamma_g$ | $\Sigma_u^+\Sigma_u^-\Gamma_u$ |
| $\Delta_u$ | | | | | | | | $\Sigma_g^+\Sigma_g^-\Gamma_g$ |

These selection rules are as follows:

$$\left.\begin{array}{ll}\text{Parallel to } a: & \Delta\Lambda = 0,\ g \longleftrightarrow u,\ + \longleftrightarrow +,\ - \longleftrightarrow - \\ \text{Perpendicular to } a: & \Delta\Lambda = \pm 1,\ g \longleftrightarrow u\end{array}\right\} \quad . \quad . \quad . \quad (4)$$

The $\Delta\Lambda$ rule is general for symmetric tops, the $gu$ rule for molecules with a centre of symmetry and the $\pm$ rule for linear molecules.

For the *trans*-bent or $C_{2h}$ model there are four species of electronic wave function, as shown, with their symmetry properties, in the left and the middle section of Table 3. The operations which serve to classify the wave functions can be taken as any two out of the following three, namely, $C_2^c$, $\sigma^{ab}$, and $i$, that is, rotation by $\pi$ around $c$, reflection across the plane $ab$, and inversion through the origin. The labels $A$ and $B$ mean symmetry and antisymmetry respectively, with respect to $C_2^c$, while $g$ and $u$ refer, as always, to $i$. The direct products are in Table 4, and from them, by comparison with the second column of Table 3, one may find the selection rules:

$$\left.\begin{array}{ll}\text{Parallel to } c: & A \longleftrightarrow A,\ B \longleftrightarrow B,\ g \longleftrightarrow u \\ \text{Perpendicular to } c: & A \longleftrightarrow B,\ g \longleftrightarrow u\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

TABLE 3. *Species of electronic and vibrational wave functions of model $C_{2h}$.*

| Elec. | $M$ | $E$ | $C_2^{\,a}$ | $\sigma^{ab}$ | $i$ | Vibs. | No. | $T$, $R$ |
|---|---|---|---|---|---|---|---|---|
| $A_g$ | — | 1 | 1 | 1 | 1 | $A_g$ | 3 | $R_g$ |
| $A_u$ | $M_c$ | 1 | 1 | −1 | −1 | $A_u$ | 1 | $T_c$ |
| $B_g$ | — | 1 | −1 | −1 | 1 | $B_g$ | 0 | $R_{ab}$ |
| $B_u$ | $M_{ab}$ | 1 | −1 | 1 | −1 | $B_u$ | 2 | $T_{ab}$ |

TABLE 4. *Direct products for model $C_{2h}$.*

| | $A_g$ | $A_u$ | $B_g$ | $B_u$ |
|---|---|---|---|---|
| $A_g$ | $A_g$ | $A_u$ | $B_g$ | $B_u$ |
| $A_u$ | | $A_g$ | $B_u$ | $B_g$ |
| $B_g$ | | | $A_g$ | $A_u$ |
| $B_u$ | | | | $A_g$ |

For the *cis*-bent model $C_{2v}$ there are again four species of electronic wave function, distinguished, as Table 5 shows, by their behaviour under any two of the operations $C_2^{\,b}$, $\sigma^{ab}$, $\sigma^{bc}$, that is, rotation by $\pi$ about $b$, and reflexion across the $ab$ plane, or across the $bc$ plane. Labels $A$ and $B$ mean respectively symmetry and antisymmetry under $C_2^{\,b}$, and subscripts 1 and 2 the same under $\sigma^{ab}$. The direct products in Table 6 lead to the following selection rules:

$$\left.\begin{array}{lccc} \text{Parallel to } b: & A \longleftrightarrow A,\ B \longleftrightarrow B & 1 \longleftrightarrow 1,\ 2 \longleftrightarrow 2 \\ \text{Parallel to } a: & A \longleftrightarrow B & 1 \longleftrightarrow 1,\ 2 \longleftrightarrow 2 \\ \text{Parallel to } c: & A \longleftrightarrow B & 1 \longleftrightarrow 2 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

TABLE 5. *Species of electronic and vibrational wave functions of model $C_{2v}$.*

| Elec. | $M$ | $E$ | $C_2^{\,b}$ | $\sigma^{ab}$ | $\sigma^{bc}$ | Vibs. | No. | $T$ | $R$ |
|---|---|---|---|---|---|---|---|---|---|
| $A_1$ | $M_b$ | 1 | 1 | 1 | 1 | $A_1$ | 3 | $T_b$ | — |
| $A_2$ | — | 1 | 1 | −1 | −1 | $A_2$ | 1 | — | $R_b$ |
| $B_1$ | $M_a$ | 1 | −1 | 1 | −1 | $B_1$ | 2 | $T_a$ | $R_a$ |
| $B_2$ | $M_c$ | 1 | −1 | −1 | 1 | $B_2$ | 0 | $T_c$ | $R_c$ |

TABLE 6. *Direct products for model $C_{2v}$.*

| | $A_1$ | $A_2$ | $B_1$ | $B_2$ |
|---|---|---|---|---|
| $A_1$ | $A_1$ | $A_2$ | $B_1$ | $B_2$ |
| $A_2$ | | $A_1$ | $B_2$ | $B_1$ |
| $B_1$ | | | $A_1$ | $A_2$ |
| $B_2$ | | | | $A_1$ |

As we shall have to consider transitions between the linear ground state of acetylene and possible bent excited states, it is important to correlate the species of the linear model with those of the bent models. Only then can we follow what happens to states of a given species of the $D_{\infty h}$ model when the hybridisation changes, in particular, into what species of states of the $C_{2h}$ or of the $C_{2v}$ model they will go. For this purpose we determine, by comparison of Tables 1, 3, and 5, for each species of the $D_{\infty h}$ model, how it behaves under

TABLE 7. *Correlation of $D_{\infty h}$ species with $C_{2h}$ species and with $C_{2v}$ species (not of $C_{2h}$ with $C_{2v}$ species).*

| $C_{2h}$ | $D_{\infty h}$ | $C_{2v}$ | $C_{2h}$ | $D_{\infty h}$ | $C_{2v}$ |
|---|---|---|---|---|---|
| $A_g$ | $\Sigma_g^+$ | $A_1$ | $A_g + B_g$ | $\Pi_g, \Phi_g, \ldots.$ | $A_2 + B_1$ |
| $A_u$ | $\Sigma_u^-$ | $A_2$ | $A_g + B_g$ | $\Delta_g, \Gamma_g, \ldots.$ | $A_1 + B_2$ |
| $B_g$ | $\Sigma_g^-$ | $B_2$ | $A_u + B_u$ | $\Pi_u, \Phi_u, \ldots.$ | $A_1 + B_2$ |
| $B_u$ | $\Sigma_u^+$ | $B_1$ | $A_u + B_u$ | $\Delta_u, \Gamma_u, \ldots.$ | $A_2 + B_1$ |

the symmetry operations of the $C_{2h}$ and of the $C_{2v}$ model, and to what species of either model such behaviour corresponds. The resulting correlations of $D_{\infty h}$ species with $C_{2h}$ species on the one hand, and with $C_{2v}$ species on the other, are shown in Table 7. It must be emphasised that, because the correlations are not of one-to-one type throughout, the Table does not exhibit exclusive and complete correlations of $C_{2h}$ species directly with $C_{2v}$ species.

From the correlations in Table 7, and the selection rules already given for electronic transitions between states of the same model of acetylene (relations 4, 5, and 6), we are able to derive selection rules for transitions between any electronic state of the straight model $D_{\infty h}$ and electronic states of either bent model $C_{2h}$ and $C_{2v}$. The procedure is to apply to the correlated species selection rules determined by the symmetry *common* to the models. As the symmetry of the $C_{2h}$ model, and of the $C_{2v}$ model, is totally included in that of the $D_{\infty h}$ model, the electronic selection rules here to be applied to correlated species are simply those of the $C_{2h}$ and the $C_{2v}$ model (relations 5 and 6). The results of these processes are given in Table 8.

TABLE 8. *Selection rules for electronic transitions between the $D_{\infty h}$ model of acetylene and the $C_{2h}$ and the $C_{2v}$ model.*

| $C_{2h}$ | | | $D_{\infty h}$ | | $C_{2v}$ | | |
|---|---|---|---|---|---|---|---|
| $\parallel c$ | $\perp c$ | | | | $\parallel a$ | $\parallel b$ | $\parallel c$ |
| $A_u$ | $B_u$ | $\leftrightarrow$ | $\Sigma_g^+$ | $\leftrightarrow$ | $B_1$ | $A_1$ | $B_2$ |
| $A_g$ | $B_g$ | $\leftrightarrow$ | $\Sigma_u^-$ | $\leftrightarrow$ | $B_2$ | $A_2$ | $B_1$ |
| $B_u$ | $A_u$ | $\leftrightarrow$ | $\Sigma_g^-$ | $\leftrightarrow$ | $A_2$ | $B_2$ | $A_1$ |
| $B_g$ | $A_g$ | $\leftrightarrow$ | $\Sigma_u^+$ | $\leftrightarrow$ | $A_1$ | $B_1$ | $A_2$ |
| $A_u + B_u$ | | $\leftrightarrow$ | $\Pi_g, \Phi_g, \ldots.$ | $\leftrightarrow$ | $A_1 + B_2$ | | $A_2 + B_1$ |
| $A_u + B_u$ | | $\leftrightarrow$ | $\Delta_g, \Gamma_g, \ldots.$ | $\leftrightarrow$ | $A_2 + B_1$ | | $A_1 + B_2$ |
| $A_g + B_g$ | | $\leftrightarrow$ | $\Pi_u, \Phi_u, \ldots.$ | $\leftrightarrow$ | $A_2 + B_1$ | | $A_1 + B_2$ |
| $A_g + B_g$ | | $\leftrightarrow$ | $\Delta_u, \Gamma_u, \ldots.$ | $\leftrightarrow$ | $A_1 + B_2$ | | $A_2 + B_1$ |

(b) *Species of Lower Electronic States of Acetylene as given by the Theory of Molecular Structure.*—The electronic ground state of acetylene is known to be a singlet state of the $D_{\infty h}$ model. Its electronic configuration is written below, by using, as is customary, lower-case letters for one-electron wave functions, that is, for orbitals. Each parenthesis contains the symmetry symbol of the molecular or bond orbital, which in some cases is followed by the quantum classification of the parent atomic orbital or orbitals. The symmetry of the total electronic wave function $\psi_e$ will be the direct product of the symmetries of all those one-electron wave functions which enter $\psi_e$ as factors. It follows from the absence of odd indices, or in detail by the use of Table 2, together with the Pauli principle, that $\psi_e$ is totally symmetrical, having the species symbol (cf. Table 1) indicated on the right:

$$K^4(\sigma_g)^4{}_{CH}(\sigma_g 2s\phi)^2{}_{CC}(\pi_u 2p)^4{}_{CC} \quad . \; . \; . \; . \; . \; . \; . \; . \quad \Sigma_g^+$$

As was noted in Part I, it would seem that the lowest orbital of the $D_{\infty h}$ model into which a $\pi$ electron could be lifted would be one of two equivalent antibonding $\pi_g 2p$ orbitals one of them diagrammatically shown in Fig. 1 at (*B*). The resulting configuration is given below; and from Table 2 it can be found that electronic states $\psi_e$ of three species thus arise, as indicated on the right:

$$K^4(\sigma_g)^4{}_{CH}(\sigma_g 2s\phi)^2{}_{CC}(\pi_u 2p)^3{}_{CC}(\pi_g 2p)_{CC} \quad . \; . \; . \quad \Sigma_u^+, \Sigma_u^-, \Delta_u$$

Another 2-quantum orbital which could conceivably be entered by an electron from the $\pi_u$ shell is the antibonding counterpart, $\sigma_u 2s\phi$, of the $\sigma_g$ bonding orbital. For a reason explained in Part I, this receiving orbital, and the resulting molecular states, are expected to lie considerably higher than those already considered. The configuration and symmetry species are as follows:

$$K^4(\sigma_g)^4{}_{CH}(\sigma_g 2s\phi)^2{}_{CC}(\pi_u 2p)^3{}_{CC}(\sigma_u 2s\phi)_{CC} \quad . \; . \; . \; . \; . \; . \quad \Pi_g$$

After this we come to 3-quantum and higher orbitals, $\sigma_g 3s$, etc., the states being classifiable as Rydberg states, which we need not now discuss.

Account must be taken, however, of the possibility that two or more of the $\pi_u$ electrons might be promoted to any of the three originally unoccupied 2-quantum orbitals. The resulting group of states will lie higher in energy than the one-promotion group just discussed; but there could be overlap between the energy ranges, and hence we should consider at least the lowest set of states of the two-promotion group, namely, those given

by double entry into the lowest of the initially unoccupied orbitals. The configuration and the species are as follows :

$$K^4(\sigma_g)^4{}_{CH}(\sigma_g 2sp)^2{}_{CC}(\pi_u 2p)^2{}_{CC}(\pi_g 2p)^2{}_{CC} \quad . \quad . \quad \Sigma_g^+, \Sigma_g^-, \Delta_g, \Gamma_g$$

Suppose now that the hybridisation changes, and that the hydrogen atoms go over into the *trans*-positions of the $C_{2h}$ model. Then one $\pi_u$ orbital must become uncoupled to give, in first approximation, two non-bonding atomic orbitals of type $2sp^2$, which, in second approximation, interact to form two molecular orbitals, one weakly bonding $b_u$, and the other weakly antibonding $a_g$. Omitting normalisation, these combinations are as written below, and their symmetries follow from Table 3 by comparison with Fig. 1 (C) (Part I), first as drawn, and then with the signs of one atomic orbital reversed :

$$(2sp^2)_{C_1} - (2sp^2)_{C_2} = b_u \quad (2sp^2)_{C_1} + (2sp^2)_{C_2} = a_g$$

Large excitations apart, the electrons of the decomposed $\pi_u$ orbital must occupy two of the four places provided by these new orbitals, and the possibilities are that both go into either, and that one goes into each, to give any of three close-lying " unexcited " states, as they may roughly be called, although only one of them is the ground state, correlated with the normal state of linear acetylene. The configurations are written below, the symmetries of CC electrons with respect to the bent model being indicated by a prefixed symbol, so that, for the $\sigma$ bond, for example, $a_g\sigma_g 2sp^2$ means a molecular orbital $a_g$, derived from a bond orbital $\sigma_g$, formed from atomic orbitals, $2sp^2$; the CC subscripts are dropped. The symmetries of $\psi_e$ follow from Table 4 :

$$K^4(\sigma_g')^4{}_{CH}(a_g\sigma_g 2sp^2)^2(a_u\pi_u 2p)^2(b_u 2sp^2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad A_g$$
$$\text{,, ,, ,, ,, } (b_u 2sp^2)(a_g 2sp^2) \quad . \quad . \quad . \quad . \quad . \quad B_u$$
$$\text{,, ,, ,, ,, } (a_g 2sp^2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad A_g$$

As compared with the linear normal state of acetylene, these " unexcited " bent states are energised; and the lowest of them would not even be metastable (unless it were made so by a spin change), but would revert immediately to the linear ground state. But the bent model offers nearly non-bonding, as well as anti-bonding, receiving orbitals for excitation; for in the orbitals $b_u$ and $a_g$ there are still two vacant places. Moreover, the excitation of one of the two electrons, which after the bending of the molecule first find themselves in the new, nearly non-bonding orbitals, up to an antibonding orbital, would require less energy than if the electron had to come from a bonding orbital. The former type of excitation, that is, one of an electron from the non-disrupted $a_u\pi_u$ bonding orbital to either new nearly non-bonding orbital, $b_u$ or $a_g$, will give the lowest group of excited states, the two having the configurations and symmetries here written :

$$K^4(\sigma_g')^2{}_{CH}(a_g\sigma_g 2sp^2)^2(a_u\pi_u 2p)(b_u 2sp^2)^2(a_g 2sp^2) \quad . \quad . \quad . \quad . \quad . \quad A_u$$
$$\text{,, ,, ,, ,, } (b_u 2sp^2)(a_g 2sp^2)^2 \quad . \quad . \quad . \quad . \quad B_g$$

The other type of excitation, that from a nearly non-bonding orbital to an antibonding orbital, could employ the antibonding $\pi_g 2p$ orbital, which one can picture by supposing the orbital represented in Fig. 1 (*B*) to be turned by a right-angle about the C–C line, and then superposed on Fig. 1 (*C*). There will be two neighbouring states, depending on which nearly non-bonding orbital retains the unexcited electron :

$$K^4(\sigma_g')^2{}_{CH}(a_g\sigma_g 2sp^2)^2(a_u\pi_u 2p)^2(b_u 2sp^2)(b_g\pi_g 2p) \quad . \quad . \quad . \quad . \quad . \quad A_u$$
$$\text{,, ,, ,, ,, } (a_g 2sp^2) \text{ ,, } \quad . \quad . \quad . \quad . \quad . \quad B_g$$

These excited orbitals are expected to lie higher than the other two of the same symmetries. These orbitals could be formed from those others by taking two electrons from nearly non-bonding orbitals, and putting one into the bonding $\pi_u 2p$ orbital, and the other into the antibonding $\pi_g 2p$ orbital. Two arguments may be given for supposing that this would require a nett input of energy. First, the energy curves for the hydrogen molecule ion, which can be exactly calculated, show that a $\sigma_u 1s$ antibonding electron is energetically

more antibonding than a $\sigma_g 1s$ bonding electron is bonding. Secondly, from the viewpoint of the valency-bond method, resonance between structures $\dot{C}$–C and C–$\dot{C}$ should give more stable bonding than between structures $\dot{C}$–$\ddot{C}$ and $\ddot{C}$–$\dot{C}$ (if we neglect the effect on bonding of the nearly non-bonding electrons), because interaction between a single electron and an electron pair is repulsive : a three-electron bond is more stable than a five-electron bond.

The other 2-quantum antibonding orbital which could receive the excited electron, $\sigma_u 2sp^2$, provides the following excited electronic states :

$$K^4(\sigma_g')^4{}_{CH}(a_g\sigma_g 2sp^2)^2(a_u\pi_u 2p)^2(b_u 2sp^2)(b_u\sigma_u 2sp^2) \quad . \; . \; . \; . \; A_g$$
$$,, \quad ,, \quad ,, \quad ,, \quad (a_g 2sp^2) \quad ,, \quad . \; . \; . \; . \; B_u$$

Taking account as before of the lowest set of two-promotion states, we find that it has only one member, and arises when the two bonding $a_u\pi_u$ electrons are elevated to the two vacant places in the nearly non-bonding orbitals :

$$K^4(\sigma_g')^4{}_{CH}(a_g\sigma_g 2sp^2)^2(b_u 2sp^2)^2(a_u 2sp^2)^2 \quad . \; . \; . \; . \; . \; . \; A_g$$

The other bent model $C_{2v}$ furnishes a similar pattern of 2-quantum states. By putting the evicted tenants of the converted orbital into the lowest of the conversion-product orbitals, we obtain three " unexcited " states :

$$K^4(\sigma_g')^4{}_{CH}(a_1\sigma_g 2sp^2)^2(b_2\pi_u 2p)^2(a_1 2sp^2)^2 \quad . \; . \; . \; . \; . \; . \; A_1$$
$$,, \quad ,, \quad ,, \quad ,, \quad (a_1 2sp^2)(b_1 2sp^2) \quad . \; . \; . \; . \; . \; B_1$$
$$,, \quad ,, \quad ,, \quad ,, \quad (b_1 2sp^2)^2 \quad . \; . \; . \; . \; . \; . \; . \; A_1$$

Promotion of an electron from the bonding $\pi$ orbital to a nearly non-bonding orbital produces two excited states :

$$K^4(\sigma_g')^4{}_{CH}(a_1\sigma_g 2sp^2)^2(b_2\pi_u 2p)(a_1 2sp^2)^2(b_1 2sp^2) \quad . \; . \; . \; . \; . \; A_2$$
$$,, \quad ,, \quad ,, \quad ,, \quad (a_1 2sp^2)(b_1 2sp^2)^2 \quad . \; . \; . \; . \; . \; B_2$$

Two more result from the promotion, alternatively, of a nearly non-bonding electron to the antibonding $\pi$ orbital,

$$K^4(\sigma_g')^4{}_{CH}(a_1\sigma_g 2sp^2)^2(b_2\pi_u 2p)^2(a_1 2sp^2)(a_2\pi_g 2p) \quad . \; . \; . \; . \; . \; A_2$$
$$,, \quad ,, \quad ,, \quad ,, \quad (b_1 2sp^2) \quad ,, \quad . \; . \; . \; . \; . \; B_2$$

and still two more, if the anti-bonding $\sigma$ orbital receives the electron :

$$K^4(\sigma_g')^4{}_{CH}(a_1\sigma_g 2sp^2)^2(b_2\pi_u 2p)^2(a_1 2sp^2)(b_1\sigma_u 2sp^2) \quad . \; . \; . \; . \; B_1$$
$$,, \quad ,, \quad ,, \quad ,, \quad (b_1 2sp^2) \quad ,, \quad . \; . \; . \; . \; A_1$$

Another state results, if we put both the $b_u\pi_u$ electrons into the two vacant places in the nearly non-bonding orbitals :

$$K^4(\sigma_g')^4{}_{CH}(a_1\sigma_g 2sp^2)^2(a_1 2sp^2)^2(b_1 2sp^2)^2 \quad . \; . \; . \; . \; . \; A_1$$

Using Table 7, we may correlate the linear with the bent states of acetylene, as in Fig. 3, in which the energy spacings, although largely arbitrary, reproduce the qualitative considerations already mentioned. As to the $D_{\infty h}$ states, we have the guidance of Ross's recent calculations (*Trans. Faraday Soc.*, 1952, **48**, 973), without which we would not know, for example, how to place the lower two-promotion states relatively to the higher one-promotion states. The " unexcited " $C_{2v}$ states are raised relatively to the corresponding set of $C_{2h}$ states, mainly because we know from vibration frequencies (next Section) that about twice as much force is needed to bend the normal acetylene molecule in the direction of the *cis*-model as to bend it towards the *trans*-model.

With the aid of Table 8 one can indicate which bent upper states are allowed to combine with the linear ground state of acetylene, and, using relations (4), which upper states become allowed only in consequence of the bending. This is done in Fig. 3 by the notes in parentheses, giving the direction of the electronic oscillation accompanying transition from the ground states to the various excited states.

### (3) Vibronic states and transitions

(a) *Classification of Vibrational Wave Functions and Vibrations; Ground-state Vibrational Energies.*—Total-vibrational wave functions $\psi_v$ will contain parameters of $\psi_e$, and thus will be different in different electronic states. However, the factorisation which led to the isolation of $\psi_v$ implies that its symmetry classification is the same for all $\psi_e$. Furthermore, the system of classification of $\psi_v$ will be the same as that of $\psi_e$: for, although the first is a function of nuclear *displacements* and the second a function of electron *positions*, both can retain or lose the various symmetry elements of the models, that is, behave in the same way under transformations of the internal axes *a*, *b*, *c*. So it comes about that we have already given the symmetry classification of $\psi_v$ for the three acetylene models, in the centre and right-hand portions of Tables 1, 3, and 5.

A total-vibrational wave function $\psi_v$ is taken as the product of all the $n$ harmonic-oscillator wave functions $\psi_m(v_m)$, one for each vibrational degree of freedom, each being that

Fig. 3. *Correlation of lower electronic states of the $D_{\infty h}$ model with those of the $C_{2h}$ and $C_{2v}$ models of acetylene. The upper states of transitions which are allowed with the ground state are marked to indicate the directions of electronic oscillations.*

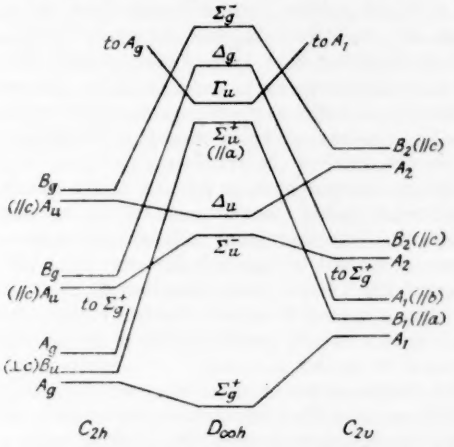
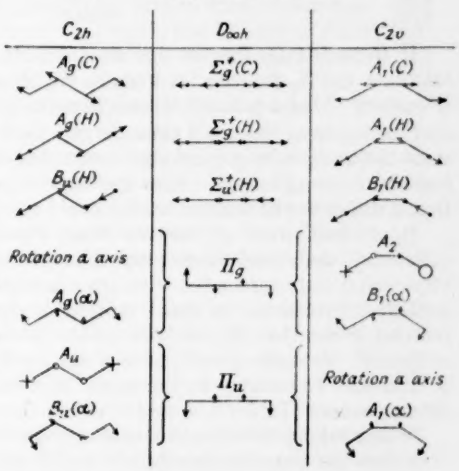



Fig. 4. *Correlation of vibrations of the three acetylene models.*




function of the vibrational co-ordinate $\sigma_m$ which corresponds to the quantum number $v_m$ of the vibration:

$$\psi_v = \psi_1(v_1) \cdot \psi_2(v_2) \ldots \psi_m(v_m) \ldots \psi_n(v_n)$$

The species of $\psi_v$ is thus the direct product of the species of all the $\psi_m$, and, if the latter are known, can be obtained from Tables 2, 4, and 6. The species of $\psi_m$ depends on the quantum number $v_m$: if the latter is zero, $\psi_m$ is totally symmetrical; if unity, then $\psi_m$ has the species of the vibrational co-ordinate; and if $m$, then the species of $\psi_m$ is the direct product of $m$ factor-species, each one that of the vibrational co-ordinate. The symmetry species of the vibrational co-ordinates of the three acetylene models are indicated by the positions of the non-zero entries in the second columns of the right-hand parts of Tables 1, 3, and 5. The figures there inserted show how many different vibrations have co-ordinates belonging to the various species; though in reading Table 1, it has to be remembered that each Π vibration has two orthogonal co-ordinates. How such numbers of vibrations may be calculated has been illustrated before (cf. *J.*, 1936, 971). When the linear molecule becomes bent, one co-ordinate of a Π vibration becomes the co-ordinate of a rotation: the symmetry species of rotations, and of translations, are indicated in the last columns of Tables 1, 3, and 5. Some symmetry species contain no individual vibrations, but all will contain total vibrational wave functions $\psi_v$ involving the simultaneous excitation of several vibrations. Total-vibrational wave functions of the degenerate species, Π, Δ, Φ, etc., are associated

with 1, 2, 3, etc., units $h/2\pi$ of vibrational angular momentum about the axis $a$ ($l$ = 1, 2, 3, etc.).

Knowing the numbers of vibrations in the various symmetry species, and also the correlation of species, given in Table 7, among the acetylene models, we can correlate the individual vibrations of these models, as is done in the approximate graphical representation of Fig. 4.

For the characterisation of any upper electronic state of acetylene from ultra-violet spectra, we require a complete knowledge of the frequencies of the vibrations of the ground state. This information is available for acetylene and dideuteroacetylene, and the figures we have used are in Table 9: they were obtained from infra-red spectra, some as fundamentals and some as difference frequencies, by Bell and Nielsen (*J. Chem. Phys.*, 1950, **18**, 1382) and Talley and Nielsen (*Phys. Review*, 1951, **82**, 338).

TABLE 9. *Fundamental vibration frequencies (cm.$^{-1}$) of the linear ground state of acetylene and of dideuteroacetylene.*

| Vibrations | $\Sigma_g^+$(C) | $\Sigma_g^+$(H) | $\Sigma_u^+$(H) | $\Pi_g$ | $\Pi_u$ |
|---|---|---|---|---|---|
| $C_2H_2$ ..... | 1974·0 | 3373·2 | 3282·5 | 613·3 | 730·74 |
| $C_2D_2$ ..... | 1764·9 | 2701·84 | 2439·1 | 511·38 | 538·66 |

If from the $\Pi_g$ frequencies we compute a bending force constant, and then try to calculate the $\Pi_u$ frequencies from it, we obtain 500 cm.$^{-1}$ for $C_2H_2$ and 360 cm.$^{-1}$ for $C_2D_2$ (Herzberg, " Infra-red and Raman Spectra," van Nostrand, New York, 1945, p. 180). The real values, more than $\sqrt{2}$ times larger, show that the energy curve from the linear ground state to the *cis*-bent ground state must *start* more than twice as steeply as the curve to the *trans*-bent ground state. How the curves continue we do not know, though it is unlikely that a difference of anharmonicity could reverse the order of the gradients.

(b) *Classification of Vibronic Wave Functions.*—In preparation for the study of the symmetry and combining properties of rotational levels, which may belong to any vibrational state associated with any electronic state, it is convenient to be able to assign a collective symmetry to the " vibronic " state, described by $\psi_{ev} = \psi_e\psi_v$ (eqn. 2). This relation shows that, for any one molecular model, the vibronic wave function $\psi_{ev}$ must be subject to the same classification of species (Tables 1, 3, and 5) as that which is common to $\psi_e$ and $\psi_v$. It follows, furthermore, that the species of any particular $\psi_{ev}$ is simply the direct product (Tables 2, 4, and 6) of the species of its factors $\psi_e$ and $\psi_v$.

When taking direct products of species of $\psi_e$ and $\psi_v$ of the linear model, one necessarily combines the quantum numbers $\Lambda$ and $l$, which measure the components, respectively, of electronic and degenerate-vibrational angular momentum around the $\infty$-fold axis $a$. Each quantum number, when not zero, is the magnitude of numbers that can have either sign, their common magnitude covering a doubly degenerate state. Hence their combined value $K$, to which the same convention applies, is given by

$$K = |\Lambda \pm l| \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

(c) *Selection Rules and Intensities of Vibronic Transitions.*—It follows from the correspondence between the systems of classifications of $\psi_{ev}$ and $\psi_e$ that the selection rules for transitions between particular vibronic states, that is, those governing the appearances of individual bands, are the same in general form as those for transitions between electronic states, that is, those which determine the occurrence of band-systems.

For transitions between vibronic states of the linear model of acetylene, allowance must be made for vibrational contributions to the angular momentum about $a$, and thus relations (4) must be rewritten, as at (8), with $K$, defined by equation (7), replacing $\Lambda$:

$$\left.\begin{array}{ll} \| \; a: & \Delta K = 0,\ g \longleftrightarrow u,\ + \longleftrightarrow +,\ - \longleftrightarrow - \\ \perp \; a: & \Delta K = \pm 1,\ g \longleftrightarrow u \end{array}\right\} \quad . \quad . \quad . \quad . \quad (8)$$

To transitions between vibronic states of the *trans*-bent model, relations (5) apply without modification, except with respect to the interpretation of the species labels. To transitions between vibronic states of the *cis*-bent model, relations (6) similarly apply.

The correlation of vibronic species between the straight and the bent models of acetylene, is exactly the same as the correlation of electronic species, given in Table 7. This, together with the principle that selection rules for vibronic, as for electronic, transitions, between states of different molecular models, are to be deduced by treating as total symmetry what is common to the combining models, determine that the selection rules for vibronic transitions between states of the straight model and those of either bent model will be as given in Table 8.

The above discussion is an application of the symmetry aspect of the Franck–Condon principle, as generalised for application to polyatomic molecules by Herzberg and Teller (*Z. physikal. Chem.*, **1933**, **21**, *B*, 410). The extended principle tells us what vibrations may change their quantum numbers, and by how much, and with what transition probability, during an electronic transition, thus contributing bands of varying intensity to the band system.

In an allowed band system, $\psi_e''\psi_e'$ belongs to a certain symmetry species. A band is allowed in this system, if $\psi_{ev}''\psi_{ev}'$ belongs to the same species, that, is, if $\psi_v''\psi_v'$ has total symmetry. In absorption at temperatures not too high, nearly all the transitions start from the vibrationless ground state, $\psi_e''\psi_v''(0)$, in which $\psi_v''(0)$ has total symmetry; and therefore in this case the condition for the appearance of a band is that the upper vibrational state $\psi_v'$ has total symmetry. Thus, only totally symmetrical vibrations can suffer unrestricted quantum changes, and so give rise to progressions, $0 \longleftarrow 0$, $1 \longleftarrow 0$, $2 \longleftarrow 0$, . . ., in the upper-state frequency. Non-totally symmetrical vibrations may be excited as even harmonics in the upper electronic state, $2 \longleftarrow 0$, etc., but only with low intensity.

If the temperature is high enough for collisions to excite vibrations in the lower electronic state, other band-series may appear. Totally symmetrical vibrations may yield progressions such as $0 \longleftarrow 0$, $0 \longleftarrow 1$, $0 \longleftarrow 2$, . . ., in their lower-state frequencies; and any vibration may produce a sequence without quantum change, $0 \longleftarrow 0$, $1 \longleftarrow 1$, $2 \longleftarrow 2$, . . ., in the difference between its frequencies in the two electronic states. All these combinations give total symmetry to $\psi_v''\psi_v'$.

When the allowed electronic transition takes place between states belonging to molecular models of different symmetry, then total symmetry, as used in the two preceding paragraphs, must be taken as the common symmetry of the combining models. In our problem, this is the symmetry of either bent model, which is fully included in that of the straight model.

Quantitatively, band intensities are given by the product of the molecular population of the initial vibrational state, the transition probability, and the magnitude of the involved energy quantum. As to the first factor, the proportion of molecules in the vibrationless state is $1/Q$, where $Q$ is the partition function. Relatively to the population of the vibrationless state, the populations of the vibrationally excited initial states are given by Boltzmann factors $ge^{-E/kT} = ge^{-\nu/0{\cdot}695T}$, where $g$ is the degeneracy of the vibrational state, and $\nu$ is in cm.$^{-1}$. The intensities of vibronic transitions starting from the vibrationless state depend little on temperature, relatively to transitions from vibrating states: the latter are strengthened by heating, the more so the higher the initial vibrational energy.

The calculation of vibronic transition probabilities, and thus of the intensities of the bands of a band-system, was first carried through for a diatomic molecule by Hutchisson in the example of hydrogen (*Phys. Review*, 1930, **36**, 410). More recently, the corresponding calculation for the polyatomic molecule, benzene, has been accomplished by Craig (*J.*, 1950, 2146). In the present study of acetylene, we shall be concerned with the distribution of intensity within a progression of bands due to transitions which, as shown by temperature effects, start from the vibrationless ground state, and end on a series of states of quantum number $v$ of a totally symmetrical vibration $m$ of the upper electronic state. For any band $v \longleftarrow 0$ of this progression, the Einstein absorption coefficient is

$$(8\pi^3/3h^2)[\int\psi_e''M\psi_e'\mathrm{d}\sigma_{\mathrm{elec.}} \cdot \int\psi_v''(0)\psi_v'(m, v)\mathrm{d}\sigma_{\mathrm{nucl.}}]^2$$

and thus the intensity distribution among the bands is given by

$$K(\nu_{0v}/\nu_{00})[\int\psi_m''(0)\psi_m'(v)\mathrm{d}\sigma_m]^2 = K(\nu_{0v}/\nu_{00})(S^v{}_{0v})^2 \quad . \quad . \quad . \quad . \quad (9)$$

where the ν's are frequencies of the vibronic transitions * $v \leftarrow 0$ and $0 \leftarrow 0$, and the constant $K$ includes the electronic transition probability, the integrals in the co-ordinates of vibrations whose quantum numbers do not change, the molecular population factor, and universal constants. Apart from the only slightly varying ratio of vibronic energy quanta, $\nu_{0v}/\nu_{00}$, intensity distribution in the progression is governed by the overlap integral, $S^q_{0v}$, which in turn depends on the separation $q$ of the origins of the co-ordinates of the lower- and upper-state vibrations $m$. For the purpose of expressing $S^q_{0v}$ as a function of $q$, we have made the simplifying assumption of treating the CH groups as "compound atoms," thus neglecting the motion of hydrogen relatively to carbon. This was one of the several sets of assumptions used by Craig, who, on this basis, gives $S^q_{0v}$ in the following form :

$$\left.\begin{aligned} S^q_{0v} &= e^{-\beta_1[q^2/2(1+\rho)]}\sum_r\left(\frac{\sqrt{\beta_2}q\rho}{1+\rho'}\right)^{v-r}\left\{\frac{v!}{r!\,(v-r)!}\right\}^{\frac{1}{2}}\left\{\frac{2^{v-r}}{(v-r)!}\right\}^{\frac{1}{2}}S^0_{0r} \\ S^0_{0r}\ (\text{even } r) &= \frac{1}{(r/2)!}\sqrt{\frac{r!}{2^r}}\left(\frac{2\sqrt{\rho}}{1+\rho}\right)^{\frac{1}{2}}\left(\frac{1-\rho}{1+\rho}\right)^{r/2};\ S^0_{0r}\ (\text{odd } r) = 0 \end{aligned}\right\} \quad . \quad . \quad (10)$$

Here $\rho = \beta_1/\beta_2 = \nu_1/\nu_2$, the subscripts 1 and 2 referring respectively to the lower and upper electronic states, and the oscillator constant $\beta = (2\pi/h)\sqrt{\mu k}$, where $\mu$ is the "reduced mass," and $k$ the force constant of the oscillator, whose frequency is ν, so that $k = 4\pi^2\nu^2\mu$. Equations (9) and (10) together give the distribution of intensity among the bands as a function of $q$; and, having measured the intensities of a number of the bands, one can choose $q$ to fit the distribution, thereby obtaining, not only a geometrical parameter of the upper electronic state, but also a means of computing, as described below, the intensity of the whole electronic transition (even if partly obscured by overlapping) from observations on a few of its bands.

With respect to the $v$th band, what is measured is the optical density $D_L$, at a series of frequencies ν within the band, and hence the optical density integral $\int D_L d\nu$ taken over the band, for an absorption-path $L$ defined as in Part II (p. 2707). The intensity is then calculated as the absorption-coefficient integral $\int \alpha d\nu$, which, Beer's law being obeyed, is independent of $L$. Finally, it is re-expressed, conventionally, as an oscillator strength :

$$f_v = (mc^2/\pi Ne^2)(\int \alpha d\nu)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Here $m$ and $e$ are the mass and charge of an electron, $c$ is the velocity of light, and $N$ is the number of molecules per cm.$^3$ in the vibrationless ground state, at the temperature of the measurement, but at the density the gas would have at 0° and 1 atm. For acetylene at 0°, the partition function $Q$ is 1·14, so that $N = 2{\cdot}36 \times 10^{19}$, and therefore the first factor in parentheses in eqn. (11), for temperatures near 0°, has the value $4{\cdot}78 \times 10^{-8}$ cm.$^2$.

In order to obtain the intensity of the whole electronic transition from the measured intensity of the $v$th band, we can use the sum rule :

$$\sum_{v=0}^{\infty}(S^q_{0v})^2 = 1$$

If we disregard the weaker combinations of the vibrationless ground state, that is, its combinations with vibrations other than the $m$th of the upper electronic state, and if we also neglect the effect on intensity distribution of the proportionately small change in $\nu_{0v}$ between the $v$th band and the most intense part of the progression, it follows from this rule that the oscillator-strength of the whole electronic transition is given by the relation

$$f = f_v/(S^q_{0v})^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The numerator on the right-hand side having been measured, and the denominator calculated, following the estimation of $q$, each measured band should give the same value of $f$, for the whole electronic transitions. It should be emphasised that intensity measurements, like the calculations based on them, are only approximate, but are nevertheless of value because spectroscopic intensities vary so widely.

* Prof. Craig asks us to mention that, although $(\nu_n/\nu_0)^4$ is inadvertently written in his formula (4), his calculations were made with the correct formula containing only the first power of $(\nu_n/\nu_0)$.

### (4) Gyrovibronic states and transitions

(a) *Classification of Rotational Wave Functions: Rotational Energies.*—Rotational wave functions contain parameters of the vibronic states with which they are associated, but this does not affect the principles of their classification. They are classed, first, with respect to their behaviour under rotations of the external axes, $X$, $Y$, $Z$, and, secondly, for any given molecular model, under those transformations of the internal axes, $a$, $b$, $c$, to which the rotational wave equation is invariant.

Rotations of the external axes lead to the familiar classification of $\psi_r$ according to the values $J = 0, 1, 2, \ldots$, each $J$ with $(2J + 1)$-fold degeneracy, where $J$ is the number of units $\hbar/2\pi$ of total angular momentum, including any supplied by electronic orbital motion and by degenerate vibrations. This is one way in which $\psi_r$ may depend on $\psi_{ev}$. Apart from one exception, the selection rule

$$\Delta J = -1, 0, +1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

holds, and accounts for the usual division of bands into P, Q, and R branches, respectively. The exception relates to linear molecules, and it is that, in transitions between two vibronic states both having $K = 0$ (two $\Sigma$ states), the allowed $J$ combinations are reduced to

$$\Delta J = -1, +1 \quad (\text{for } \Sigma - \Sigma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

so that the bands, which by equations (8) are of " parallel " type, have no Q branches.

The rotational wave equation of the $D_{\infty h}$ model is invariant to the transformations of $a$, $b$, $c$, summarised in the symbol $D_\infty$; and thus $\psi_r$ may be, in this case, classified according to its behaviour under rotations $C^a_\phi$ by $\pm\phi$ round $a$, and $C_2^{bc}$ by $\pi$ round $b$ or $c$, as shown in Table 10. The species are labelled $\Sigma$, $\Pi$, $\Delta$, . . ., according as $K$, the number of units of vibronic angular momentum about $a$, is 0, 1, 2, . . . In this respect also $\psi_r$ is dependent on $\psi_{ev}$. The two non-degenerate $\Sigma$ species together cover, and each degenerate species, $\Pi$, $\Delta$, etc., separately covers, all possible values of $J$, which, as a measure of total angular momentum, cannot be less than $K$, the measure of its figure-axial component. The direct products of Table 11, in combination with the species of the electric moment $M$ in Table 10, give the selection rules:

$$\text{Parallel to } a: \Delta K = 0. \quad \text{Perpendicular to } a: \Delta K = \pm 1 \quad . \quad . \quad . \quad . \quad (15)$$

Table 10. *Species of rotational wave functions of $D_{\infty h}$ model.*

| Rotn. | $K$ | $M$ | $E$ | $2C_\phi{}^a$ | $C_2{}^{bc}$ |
|---|---|---|---|---|---|
| $\Sigma_1$ (even $J$) | 0 | — | 1 | 1 | 1 |
| $\Sigma_2$ (odd $J$) | 0 | $M_a$ | 1 | 1 | −1 |
| $\Pi$ (all $J$) | 1 | $M_{bc}$ | 2 | $2\cos\phi$ | 0 |
| $\Delta$ (all $J$) | 2 | — | 2 | $2\cos 2\phi$ | 0 |
| . . . (all $J$) | . . . | . . . | . . . | . . . | . . . |

Table 11. *Direct products of rotation species $D_\infty$ of $D_{\infty h}$ model.*

| | $\Sigma_1$ | $\Sigma_2$ | $\Pi$ | $\Delta$ |
|---|---|---|---|---|
| $\Sigma_1$ | $\Sigma_1$ | $\Sigma_2$ | $\Pi$ | $\Delta$ |
| $\Sigma_2$ | | $\Sigma_1$ | $\Pi$ | $\Delta$ |
| $\Pi$ | | | $\Sigma_1\Sigma_2\Delta$ | $\Pi\Phi$ |
| $\Delta$ | | | | $\Sigma_1\Sigma_2\Gamma$ |

The rotational wave equation for *both* the bent models $C_{2h}$ and $C_{2v}$ is invariant to those transformations of the internal axes which are denoted by $V$; and thus the species of $\psi_r$ depend on its behaviour under rotations by $\pi$ round any two of the axes $a$, $b$, and $c$, as shown in Table 12. Symmetry under all three rotations is denoted by $A$, and under one only by $B$ with the appropriate subscript. The direct products in Table 13, together with the electric-moment species in Table 12, give the selection rules:

$$\| a: A \longleftrightarrow B_a, B_b \longleftrightarrow B_c \quad \| b: A \longleftrightarrow B_b, B_c \longleftrightarrow B_a \quad \| c: A \longleftrightarrow B_c, B_a \longleftrightarrow B_b \} \quad . \quad (16)$$

Table 12. *Species of rotational wave functions of the $C_{2h}$ and $C_{2v}$ models.*

| Rotn. | $M$ | $E$ | $C_2{}^a$ | $C_2{}^b$ | $C_2{}^c$ |
|---|---|---|---|---|---|
| $A$ | — | 1 | 1 | 1 | 1 |
| $B_a$ | $M_a$ | 1 | 1 | −1 | −1 |
| $B_b$ | $M_b$ | 1 | −1 | 1 | −1 |
| $B_c$ | $M_c$ | 1 | −1 | −1 | 1 |

Table 13. *Direct products of rotation species $V$ of the $C_{2h}$ and $C_{2v}$ models.*

| | $A$ | $B$ | $B_b$ | $B_c$ |
|---|---|---|---|---|
| $A$ | $A$ | $B_a$ | $B_b$ | $B_c$ |
| $B_a$ | | $A$ | $B_c$ | $B_b$ |
| $B_b$ | | | $A$ | $B_a$ |
| $B_c$ | | | | $A$ |

By examining the behaviour of the rotational species of the $D_{\infty h}$ model (Table 10) with respect to the symmetry operations determining the rotational species of the $C_{2h}$ and the $C_{2v}$ models (Table 12), we can correlate the two sets of species, as is done in Table 14. If now, in the light of this correlation, we compare the selection rules (15) and (16), in order to discover what is common between them, or, in other words, derive selection rules for the combination of rotational states of the straight model with those of either bent model, we find the results summarised in Table 15.

TABLE 14. *Correlation of rotational species among the $D_{\infty h}$, $C_{2h}$ and $C_{2v}$ models.*

| | | | | |
|---|---|---|---|---|
| Symmetric top (model $D_{\infty h}$) ..... | $\Sigma_1$ | $\Sigma_2$ | $\Pi$, $\Phi$, etc. | $\Delta$, $\Phi$, etc. |
| Asymmetric top (models $C_{2h}$ and $C_{2v}$) ..... | $A$ | $B_a$ | $B_b + B_c$ | $A + B_a$ |

TABLE 15. *Rotational selection rules for transitions between the $D_{\infty h}$ model of acetylene and either the $C_{2h}$ or $C_{2v}$ models.*

| | $C_{2h}$ or $C_{2v}$ | | |
|---|---|---|---|
| $D_{\infty h}$ | $\parallel a$ | $\parallel b$ | $\parallel c$ |
| $\Sigma_1$ ..... | $B_a$ | $B_b$ | $B_c$ |
| $\Sigma_2$ ..... | $A$ | $B_c$ | $B_b$ |
| $\Pi$ ..... | $B_b$, $B_c$ | $A$, $B_a$ | $A$, $B_a$ |
| $\Delta$ ..... | $A$, $B_a$ | $B_b$, $B_c$ | $B_b$, $B_c$ |

The energy levels of the linear model, considered as a rigid symmetric top, are given by the formula

$$E = BJ(J+1) + (A-B)K^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If $E$ is to be expressed in cm.$^{-1}$, then $A = \boldsymbol{h}/8\pi^2\boldsymbol{c}I_a$ and $B = \boldsymbol{h}/8\pi^2\boldsymbol{c}I_b$, the constant $\boldsymbol{h}/8\pi^2\boldsymbol{c}$ having the value $27{\cdot}983 \times 10^{-40}$ g.-cm.

Because of the relative lightness of hydrogen, both the bent acetylene models, although they are asymmetric tops, will be nearly symmetric tops, so that an analogous energy formula, containing the average of $B$ and $C$ in place of either, will apply approximately:

$$E = \tfrac{1}{2}(B+C)J(J+1) + \{A - \tfrac{1}{2}(B+C)\}K^2 \quad . \quad . \quad . \quad . \quad (18)$$

when $C = \boldsymbol{h}/8\pi^2\boldsymbol{c}I_c$. However, the precise formula for the asymmetric top, supposed rigid, is

$$E = \tfrac{1}{2}(A+C)J(J+1) + \tfrac{1}{2}(A-C)E(\kappa) \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where $\kappa$ is a parameter measuring the degree of asymmetry,

$$\kappa = (2B - A - C)/(A - C)$$

and $E(\kappa)$ is the energy quantity (Ray's modification of the Wang function) which has been evaluated by King, Hainar, and Cross (*J. Phys. Chem.*, 1943, **11**, 27; 1949, **17**, 826) for all $J$, $K$ values up to $J = 12$ ($K = 0, 1, \ldots J$, and $J = K, K+1, \ldots 12$).

For analysis of the rotational structure of bands due to transitions from the normal electronic state of acetylene, we need information concerning the moments of inertia $B$ of the latter, which depend on $I_b$, and thus on the internuclear distances. These quantities are evaluated by the rotational analysis of infra-red bands of $C_2H_2$ and $C_2D_2$, and we have used the data in Table 16, furnished by Saksena's recent studies of bands in the photographic infra-red (*J. Chem. Phys.*, 1952, **20**, 95).

TABLE 16. *Dimensions of acetylene at zero-point energy in its normal electronic state.*

| | $B$ (cm.$^{-1}$) | $I_b$ ($10^{-40}$ g.-cm.$^2$) | $r_{CC}$ (Å) | $r_{CH}$ (Å) |
|---|---|---|---|---|
| $C_2H_2$ ..... | 1·1769 | 23·776 | 1·208 | 1·058 |
| $C_2D_2$ ..... | 0·8479 | 33·004 | | |

(b) *Classification and Correlation of Gyrovibronic States of the Three Models of Acetylene.*—In his papers on the theory of transitions between straight and bent states of a triatomic molecule (*locc. cit.*), Mulliken showed that, even when the atomic masses are of the same order of magnitude, a fairly large bending angle will still allow the resulting asymmetric top to obey approximately the $K$-containing energy formulæ of the symmetric top, thus justifying description as a prolate near-symmetric top. This must be still more true of a

molecule, such as acetylene, in which bending only moves light atoms off the line of considerably heavier ones: indeed, acetylene must be a prolate near-symmetric top independently of the bending angle. Thus for either bent model of acetylene, a quantity $K$ exists with approximate significance as a quantum number measuring the angular momentum about $a$, though it can be defined exactly only by the limit to which it goes as the bent molecule is straightened. In the last stages of this imaginary process, the angular momentum will pass over from being carried by rotation and described in $\psi_r$, to being carried by the electronic motion, or by degenerate vibrations, and described in $\psi_{ev}$. However, the component of angular momentum itself will experience no discontinuity, but will merely become more definite, as the straightening process goes to completion.

As can be seen from Table 7 (p. 2711) in its application to vibronic states, any vibronic state of either bent model is correlated with an infinite series of vibronic states of the straight model: they differ with respect to angular momentum about $a$, that is, with respect to $K$. For example, a vibronic $A_g$ state of the *trans*-bent model is correlated with

FIG. 5. *Rotational, gyrovibronic, and overall classification of energy levels of the* $C_{2h}$ *model of acetylene: correlation with the* $D_{\infty h}$ *model.*

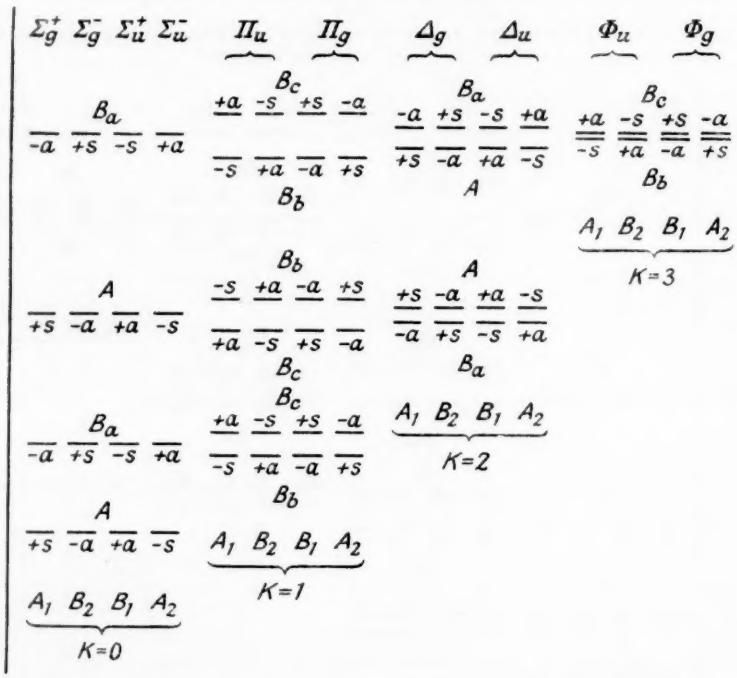
linear $\Sigma_g^+$ $\Pi_g$, $\Delta_g$, . . ., states for which $K = 0, 1, 2, \ldots$ The detailed meaning of this must be that to a vibronic bent state belong rotational states supplying infinitely various amounts and directions of angular momentum, which, as the molecule is straightened, converge, with respect to the component of angular momentum about $a$, on the infinitude of discrete limits, corresponding to $K = 0, 1, 2, \ldots$ Mulliken has given the name gyrovibronic state to a set of energy levels, such as those of any single column in Figs. 5 and 6, which belong to a particular vibronic state and to a particular value of $K$, whether precisely actual or defined by its limiting value. In either bent model of acetylene, one vibronic state contains infinitely many gyrovibronic states, but in the straight model, the vibronic is the same as the gyrovibronic state (because here rotation does not contribute to $K$). One bent gyrovibronic state is correlated with one linear gyrovibronic, non-degenerate state.

Two bent gyrovibronic states are correlated with one linear gyrovibronic doubly degenerate state. The correlations, which follow from Table 7, are shown by the top and the bottom sets of symbols in Figs. 5 and 6. Each gyrovibronic state of any model contains infinitely many energy levels which are distinguished with respect to $J$. The way in which the levels of pairs of bent gyrovibronic states mix and converge to give the levels of linear degenerate gyrovibronic states will be noted in the next Section.

### (5) Energy levels and their transitions

(a) *Classification of Unfactorised Wave Functions.*—As Mulliken has pointed out (*locc. cit.*), this is a useful classification, because the few " overall " selection rules to which it leads

Fig. 6. *Rotational, gyrovibronic, and overall classification of energy levels of the* $C_{2v}$ *model of acetylene : correlation with the* $D_{\infty h}$ *model.*




are strictly obeyed, even when the factorisation of $\psi$ is far from strict, as may happen in the presence of perturbations. Three groups of operations are involved.

The first consists of the infinitude of rotations of the external axes, $X$, $Y$, $Z$. This leads to the $J$ classification, already described on p. 2719. If $\psi$ is factorised, and $\psi_r$ is a factor, then care is taken of the $J$ classification in $\psi_r$. If $\psi$ is not factorised, then the $J$ classification applies without modification to $\psi$ itself.

The second " group " of operations amounts only to the inversion $I$ of external axes, $X$, $Y$, $Z$, through their origin. This process multiples the wave function either by $+1$ or by $-1$, and so gives rise to the " parity " classification of $\psi$ as $+$ or $-$. The condition under which the intensity-controlling integral $\int\psi''M\psi'd\sigma$ does not vanish, is that the integrand shall not change sign under $I$, and, since the electric moment $M$ does change sign, the product $\psi''\psi'$ must change sign also. The selection rule follows :

$$+ \longleftrightarrow - \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The remaining group of operations consists in the possible permutations of labels between sets of nuclei whose positions can be interchanged by rotation without making any physical difference. In the case of acetylene, on any of our models, there is just one such permutation, $P_2$, and this exchanges the labels of the two carbon atoms and of the two hydrogen atoms. According as $P_2$ does not or does change the sign of $\psi$, the latter is classed as symmetric $s$ or antisymmetric $a$. Since $M$ does not change sign under $P_2$, the selection rule is as follows:

$$s \longleftrightarrow s \qquad a \longleftrightarrow a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

(b) *Classification and Correlation of Energy Levels of the Three Models of Acetylene.*— It is necessary first to factorise $I$ and $P_2$, each into two operators, the first of which acts on $\psi_r$ only, while the second acts on $\psi_{ev}$ only. The factors differ according to the molecular model. For the $C_{2h}$ model the operational equations are as follows:

$$I(\psi) = C_2^c(\psi_r) \,.\, \sigma^{ab}(\psi_{ev}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$P_2(\psi) = C_2^c(\psi_r) \,.\, C_2^c(\psi_{ev}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

The first factor in (22) turns the molecule by $\pi$ around $c$. In a general case everything thus turned would have to be reflected across the plane $ab$, in order to complete the operation $I$. The second factor in (22) thus reflects the electron positions, and the nuclear *displacements*. The nuclear *positions* remain unreflected, but as they lie in the plane $ab$, no reflexion of them is needed for the completion of $I$. In equation (23), the first factor rotates the electron positions, the nuclear equilibrium positions, and the nuclear displacements, while the second restores the electron positions, and nuclear displacements, but not the nuclear positions. Thus the two operations together amount to the nuclear permutation $P_2$.

For the $C_{2v}$ model the corresponding operational equations are as follows:

$$I(\psi) = C_2^c(\psi_r) \,.\, \sigma^{ab}(\psi_{ev}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$P_2(\psi) = C_2^b(\psi_r) \,.\, C_2^b(\psi_{ev}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The justifying arguments are similar to those in the preceding paragraph. For the $D_{\infty h}$ model either pair of equations can be used, since the axes $b$ and $c$ have in this model become equivalent symmetry axes.

For any of the rotational species of the $D_{\infty h}$ model, as listed in Table 10, and for some particular $J$ and $K$, we note the correlated rotational species of the $C_{2h}$ and $C_{2v}$ models in Table 14 (p. 2720), and then find the effects of $C_2^c$ and of $C_2^b$ on such species of $\psi_r$ in Table 12 (p. 2719). These are to multiply $\psi_r$ by either $+1$ or $-1$. The effects of $\sigma^{ab}$ and of $C_2^c$ on $\psi_{ev}$ for each of the four vibronic species of the $C_{2h}$ model are then found from Table 3 (p. 2711); and likewise the effects of $\sigma^{ab}$ and of $C_2^b$ on $\psi_{ev}$ for each of the four vibronic species of the $C_{2v}$ model are found from Table 5 (p. 2711). These effects are always to multiply $\psi_{ev}$ by either $+1$ or $-1$. By multiplying the results obtained in these ways, we can find what the operators $I$ and $P_2$ will do to $\psi$, thus determining the overall species of the energy levels, as recorded in Figs. 5 and 6.

Correlation of the gyrovibronic states of either bent model, as shown below the energy levels of Figs. 5 and 6, with those of the linear model, as indicated above the columns of levels, has been discussed; but it remains to be considered how, when $K > 0$, groups of individual levels of a bent model coalesce to give degenerate levels as the molecule is straightened. It will suffice to take, as an example, the *trans*-bent model (Fig. 5), and, in particular, its gyrovibronic states $A_g$ and $B_g$, and their energy levels which have the quantum numbers $J = 1$ and $K = 1$. There are four such levels, each gyrovibronic state containing a doublet, whose separation depends on the degree of asymmetry. As the molecule straightens, so that the distinction between $b$ and $c$, $I_b$ and $I_c$, $B$ and $C$, and therefore between $B_b$ and $B_c$, becomes lost, the wave functions of the two $+s$ levels mix, either with the other, to eventual equality, as also do those of the two $-a$ levels, while at the same time the energy separation of the equally mixed $+s$ level and the equally mixed $-a$ level becomes zero, so that we now have a doubly degenerate level of the gyrovibronic state $\Pi_g$. Such mixings and convergencies occur in sets of four " bent "

levels, each set to give one degenerate " straight " level, over the whole manifold of levels for which $K > 0$.

In practice the convergencies may not be completed to coincidence, if the factors $\psi_{ev}$ and $\psi_r$ cannot accurately be separated, so that angular momentum is not sharply partitioned between rotations and degenerate vibrations ($l$-type doubling), or between rotations and electronic orbital motion ($\Lambda$-type doubling). This being taken into account, each set of four " bent " levels will yield two " straight " levels, one $s$ and one $a$, which will not be degenerate but will form a definite doublet. We may summarise such phenomena under the collective term " $K$-type doubling." It is expected to be a small effect, except where perturbations spoil the factorisation of $\psi$.

(c) *Intensities of Rotational Lines: Effects of Nuclear Spin in Acetylene and Dideutero-acetylene.*—The way in which, in any P, Q, or R branch of a band, the intensities of successive rotational lines in general rise at first with the $J$-degeneracy as $J$ increases, later to fall with the eventually dominating Boltzmann factor, presents no special features in our problem. However, the effect of nuclear spin in giving different statistical weights to the $s$ and $a$ levels, and thus leading to a superposed alternation, or other periodicity, of intensity, is deserving of comment.

In $^1H{\cdot}^{12}C{\vdots}^{12}C{\cdot}^1H$, the carbon nuclei have no spin, while each proton has the spin quantum number $\frac{1}{2}$ with 2-fold space-degeneracy, so that there are 4 nuclear-spin functions, of which 3 are symmetric and 1 antisymmetric to $P_2$ (Fowler and Guggenheim, " Statistical Thermodynamics," Cambridge Univ. Press, 1939, p. 84). The former spin functions must multiply the $\psi$ of $a$ levels, and the latter the $\psi$ of $s$ levels, in order to make the complete molecular wave function antisymmetric in (odd mass-numbered) protons. Thus the $a$ levels of $C_2H_2$ have three times the statistical weight of $s$ levels. In $^2D{\cdot}^{12}C{\vdots}^{12}C{\cdot}^2D$, each deuteron has spin quantum number 1 with 3-fold space-degeneracy, and hence there are 9 nuclear-spin functions, 6 symmetric and 3 antisymmetric, with which to make the complete wave function symmetric in (even mass-numbered) deuterons. Thus the $s$ levels of $C_2D_2$ have twice the statistical weight of the $a$ levels.

In transitions between two gyrovibronic states of the linear acetylene model, provided that at least one of the states has $K = 0$, the rotational lines of a branch of a band will alternate in intensity, in opposite ways for $C_2H_2$ and $C_2D_2$, as can be followed in detail from Fig. 5 or 6. If neither gyrovibronic state has $K = 0$, then, in the absence of $l$-type doubling, no such alternation will occur, since both combining levels will be degenerate, each having an $s$ and an $a$ component. When $l$-type doubling can be observed, there will be alternation over all lines, each doublet having a weak and a strong component.

In transitions between a gyrovibronic state of the linear model and one of either bent model, provided that in one of the states $K = 0$, similar alternations will appear; for the overall selection rules (20, 21, pp. 2722, 2723) will always exclude from combination one member of each doublet for which in the other state $K = 1$. If neither gyrovibronic state has $K = 0$, a slightly more complicated periodicity of intensities should be found. The successive $J$ values along a branch of a band will each be represented by a doublet with a stronger and a weaker component; and these components will change sides on passing from any doublet to the next. These expected relationships can easily be followed from Figs. 5 and 6; and they have diagnostic value in our analytical problem.

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## 552. *Excited States of Acetylene. Part IV.* Description and Analysis of the Near-ultra-violet Absorption Spectra of Acetylene and Dideuteroacetylene: Nature of the Excited State.*

By C. K. Ingold and G. W. King.

From the description and analysis mentioned in the title, it is concluded that the first excited state of acetylene is a *trans*-bent state, showing a completed change of σ-bond hybridisation from linear *sp* to plane-trigonal $sp^2$. A three-electron bond joins the carbon atoms, which between them have three unshared electrons in two *trans*-related orbitals. The electronic motion has the symmetry of the model, except that, as in other π-electron systems, the molecular plane is a nodal plane. Bond lengths, bond angles, and the stretching, and planar-bending force constants in excited acetylene are almost as in normal benzene.

### (1) The spectra

The near-ultra-violet spectrum of acetylene to be discussed is that of the band-system which we observe in absorption to commence very weakly at 2500 Å and to continue with markedly increasing strength to about 2100 Å, where the sudden rise in the number and confusion of the bands indicates overlap by a stronger band-system belonging mainly to the vacuum-ultra-violet. The near-ultra-violet spectrum of dideuteroacetylene is generally similar, though with many quantitative differences. The spectrum of acetylene has been described, and its analysis attempted a number of times, but without producing any agreed conclusion. The near-ultra-violet spectrum of dideuteroacetylene has not been previously recorded.†

(a) *Previous Investigations of the Spectrum of Acetylene.*—Henri and Landau believed that they described this spectrum, but most of their bands were due to impurities, and it is not even certain that any was due to acetylene (*Compt. rend.*, 1913, **156**, 697). The weakness of the acetylene spectrum makes the necessary standard of purity high. Hopfield briefly mentioned the band-system (*Phys. Review*, 1927, **29**, 356). Kistiakowsky measured a number of genuine acetylene bands, which he assigned to three progressions in 100 $cm.^{-1}$ with intervals of 1012 and 1032 $cm.^{-1}$ between the progressions; and he found continuous absorption from about 2300 Å (*ibid.*, 1931, **37**, 276). Herzberg observed the band-system, decided that intervals of 865 and 1365 $cm.^{-1}$ separated the main bands, and tentatively assigned the electronic transition to a spin-forbidden intercombination (*Trans. Faraday Soc.*, 1931, **27**, 379). Kato arranged his observed bands into progressions in 390, 418, 600, 630, and 1050 $cm.^{-1}$; and he reported that the bands were continuous, indicating predissociation (*Bull. Inst. Phys. Chem. Res., Tokyo*, 1931, **10**, 343). Price was mainly concerned with vacuum-ultra-violet band-systems, but he mentions the long-wave system of acetylene, concluding that the reported continuum beyond 2300 Å is due to impurities, and that the bands show no signs of predissociation (*Phys. Review*, 1934, **45**, 843; 1935, **47**, 444). Jonescu arranged the acetylene bands in three progressions in about 1000 $cm.^{-1}$, with intervals of 570 and 640 $cm.^{-1}$ between the progressions; and he examined the line structures of some bands, deducing that the electronic transition is of $\Sigma - \Sigma$ type (*Compt. rend.*, 1934, **199**, 710; 1935, **200**, 817), a strange conclusion inasmuch as all the stronger bands are double-headed, indicating P, Q, and R branches. Göpfert arranged the bands in many progressions in about 1000 $cm.^{-1}$ (*Z. wiss. Phot.*, 1935, **34**, 156). Woo, Liu, Chu, and Chih concluded that the spectrum contained three progressions, called A, B, and C, each in about 1050 $cm.^{-1}$, for which intensity is not increased by a reduction of temperature;

* Part III, preceding paper.

† Using acetylene with a path-length of 20 metre-atmospheres, we have explored the ultra-violet from 2500 Å to the beginning of the visible region in an unsuccessful search for a longer-wave, but weaker, band-system. Thus the band-system now to be discussed arises from the *lowest* electronic excitation detectable with our equipment.

however, they could make no assignment of the bands in accordance with selection rules, and concluded that the electronic transition is in some way forbidden (*J. Chem. Phys.*, 1938, **6**, 240). These authors usually recorded only the heads of bands, but their measurements agree well with ours. On the other hand, we do not fully confirm their work on the effect of temperature on band intensity.

From the variety, and also the reserve, in the above conclusions, almost the only agreed feature of which is that a frequency near 1000 cm.$^{-1}$ is important, it will be clear that there is nothing very obvious about the structure of the spectrum, or the lines along which it might be analysed.

(b) *General Description of the Spectrum of Acetylene.*—A section of the spectrum, as photographed at −78° and +20°, is reproduced in Fig. 7 at (*a*). From the point of view of analysis, the spectrum contains an embarrassingly large number of bands, with little obvious regularity. From 2500 to 2100 Å, the general order of band intensity increases by many hundred times; yet even at its strong end, the spectrum is some thousands of times weaker than is normal for an allowed electric-dipole transition. All the stronger bands are double headed, are shaded to red, and have well-defined rotational structures.

Although the spectrum is essentially a rich collection of bands, it seems to have a weak continuous background. This appearance is probably due, at least in part, to unresolved weak bands or overlapping tails of bands, because the lowest absorption coefficients that can be measured between the visible bands vary less regularly than would be expected of a real continuum :

| | | | | | | |
|---|---|---|---|---|---|---|
| λ (Å) ..... | 2308 | 2251 | 2232 | 2204 | 2194 | 2157 |
| ε (cm.$^{-1}$) ..... | 0·06 | 0·02 | 0·01 | 0·04 | 0·02 | 0·05 |

However, the presence of a genuine continuum, having absorption coefficients of the order of 0·01 cm.$^{-1}$ or somewhat less, is not excluded.

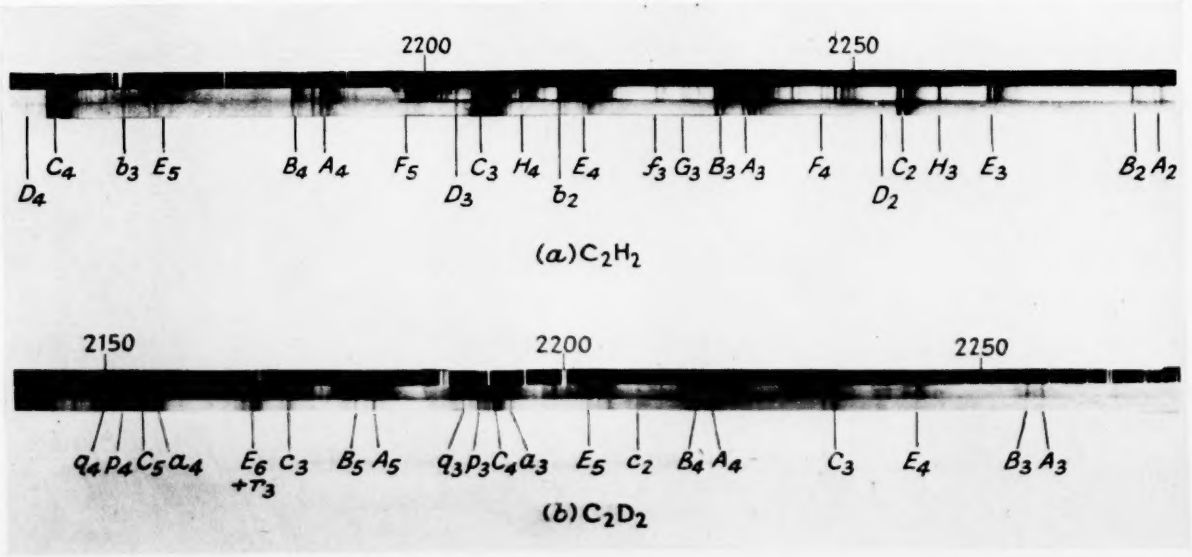
For the purpose of describing the band pattern of the spectrum, we use Woo, Liu, Chu, and Chih's labels, A, B, and C, for the three strongest progressions of bands, and supply further letter-labels for others to be described. Contrary to those authors, we find only one progression of strong bands whose intensity is not decreased by cooling the gas, namely, progression C. These bands form the main " milestones " of the spectrum, and are labelled $C_0$, $C_1$, $C_2$, . . . : we shall later justify the assumption that the first observed band $C_0$ is the theoretical origin of the progression, so that the subscripts represent the number of quanta with which the relevant upper-state vibration is excited. The interval between successive bands is about 1000 cm.$^{-1}$, but as the progression continues towards higher frequencies, the interval gradually falls. The bands have R and Q heads with a separation of about 17 cm.$^{-1}$.

Associated with each C band is a set of bands, labelled A, B, D, E, . . . . ., with the same subscript as the C band. These bands form a pattern, which, except for band D, spread out on the low-frequency side of the C band. Such a pattern is repeated about each C band, the patterns overlapping. In Fig. 8, a typical pattern of the acetylene spectrum is shown at (*A*), the entered frequency intervals being the separations of R heads. As we shall note later, the pattern is really more extended on the low-frequency side than Fig. 8 represents. The relative frequencies and intensities, and the differences in the temperature dependence of intensity, within a pattern, are generally the same for all the patterns; but the frequency intervals differ slightly from one pattern to another. It will be clear that each of the labels A, B, D, E, . . ., designates a progression to higher frequencies in about 1000 cm.$^{-1}$, the successive intervals diminishing as in the C progression.

About 40 cm.$^{-1}$ on the high-frequency side of each C band lies the D band, which is much weaker than the C band, but, like it, is not weakened by cooling. The D bands appear to have a single head.

Approximately 600 cm.$^{-1}$ to the low-frequency side of the C bands are the A and the B bands, separated by about 50—60 cm.$^{-1}$ from each other, each having an intensity roughly one-third of that of the C band. The A and the B bands are double-headed. They are diminished in intensity, but not extinguished when the gas is cooled from +20° to −78°. The interval between the D and the B bands remains almost constant at 611—

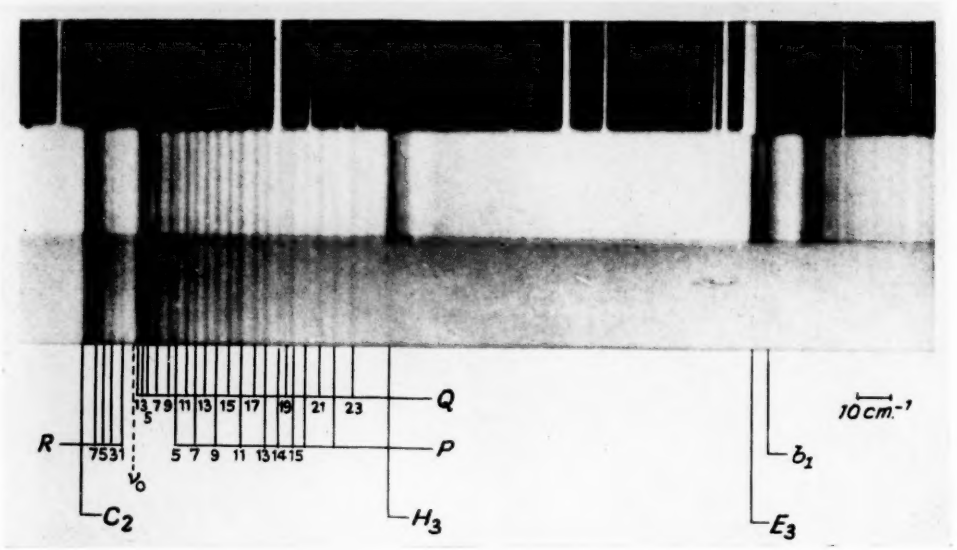
FIG. 7. *Part of the absorption spectra of acetylene and dideutero-acetylene.*




(Top) *Iron-arc comparison spectrum.*
(Central) *Absorption spectrum with gas at* $+20^{\circ}$ C.
(Bottom) *Absorption spectrum with gas at* $-78^{\circ}$ C.

[To face p. 256.

FIG. 11. *Absorption spectrum of acetylene in the region 2255—2270 Å.*




(Top) *Iron-arc comparison spectrum.*
(Central) *Absorption spectrum with gas at* + 20° C.
(Bottom) *Absorption spectrum with gas at* −78° C.

(*Rotation lines are labelled with the J-values of their lower-state energy levels.*)

613 cm.$^{-1}$ throughout the spectrum, but all the other intervals between the bands mentioned vary more widely from pattern to pattern.

The A and the B bands have very weak satellites in the G bands, which lie about 50 cm.$^{-1}$ on the high-frequency side of the B bands. The G bands are weakened by cooling the gas, in much the same way, as far as can be judged, as are the A and the B bands. Some at least of the G bands are double-headed, but with a head separation which is much narrower than that of other double-headed bands in this spectrum.

Approximately another 600 cm.$^{-1}$ to the low-frequency side of the A and B bands lie the E and the H bands, both of which are less intense, and show greater relative weakening when the temperature is reduced, than the A and the B bands. They are double-headed. The various intervals involving E and H bands vary appreciably from pattern to pattern. One very simple relation holds: it is that the separation between R-heads of the E and the H bands is always close to twice that of the A and the B bands, the one interval becoming exactly twice the other, if we use band origins instead of R-heads.

After yet another step of about 600 cm.$^{-1}$ to lower frequencies, we come to the J and the F bands, which are still weaker, and still more temperature-sensitive, disappearing

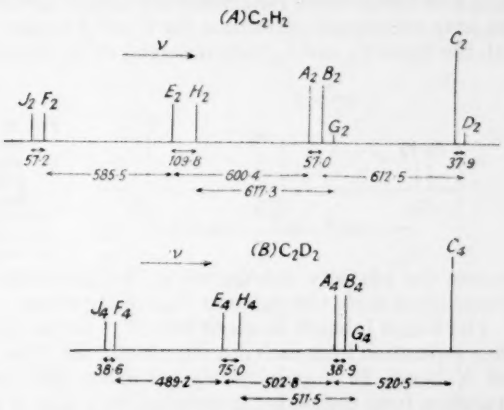



FIG. 8. *Examples of main parts of the unit-patterns, which by repetition form progressions in the absorption spectra of acetylene and dideutero-acetylene. (A) Pattern 2 of acetylene. (B) Pattern 4 of dideutero-acetylene. (The frequency separations are between R-heads in cm.*$^{-1}$.)

completely from the spectrum at −78°. They are also double-headed. The simple and exact relation here is that their frequency separation is equal to that of the A and the B bands.

Most of the spectrum so far described is repeated, much more weakly, with a shift of 1380 cm.$^{-1}$ to higher frequencies. Corresponding to the progressions A, B, C, E, F, H, and J, we find these weakened and shifted progressions, which we label a, b, c, e, f, h, and j, respectively. Bands of the progressions a, b, c, . . ., show temperature effects on intensity analogous to those of bands of the corresponding progressions A, B, C, . . .

(c) *General Description of the Spectrum of Dideuteroacetylene.*—This spectrum, a part of which is shown in Fig. 7 at (*b*), is generally similar to the spectrum of acetylene. It lies in approximately the same spectral region, but the frequency intervals are smaller, with the result that the spectrum is more compact, and that there is more overlapping of bands. Moreover, the bands themselves have a closer rotational structure, often not resolved with our equipment. The general order of band intensity is lower, and the increase of intensity towards higher frequencies is not so steep, as in the spectrum of acetylene.

The progressions A, B, C, E, F, G, H, and J, and also a, b, c, e, f, and j, are all observed in the spectrum of dideuteroacetylene. With respect to relative intensity, and the variation of intensity with temperature, all these dideuteroacetylene bands qualitatively resemble the corresponding acetylene bands, with the exception that the progressions a, b, c, . . ., are not so weak relatively to the progressions A, B, C, . . ., in this spectrum as in the acetylene spectrum. Two weak progressions, namely D and h, of the spectrum of acetylene have not been found in that of dideuteroacetylene. They are believed to be

obscured by overlapping. On the other hand, a whole new group of related weak progressions, labelled p, q, r, t, u, w, and y, have been found in the spectrum of dideutero-acetylene.

In all ascending progressions the frequency interval is about 800 cm.$^{-1}$, falling steadily towards higher frequencies. In the patterns which extend from each C band to lower frequencies, the large interval, separating the pairs or trios of more closely spaced bands, is about 500 cm.$^{-1}$, as shown in Fig. 8 at (*B*). The bands of the progressions a, b, c, e, f, and j, lie about 1300 cm.$^{-1}$ higher than corresponding bands of the progressions A, B, C, E, F, and J, respectively. The bands of the progressions, p, q, r, t, u, w, and y, lie about 2200 cm.$^{-1}$ above the correspondingly numbered bands of progressions A, B, C, E, F, H, and J, respectively.

(d) *Additional Bands appearing at Higher Temperatures.*—In photographs of the spectrum of acetylene at 200°, parts of four more weak progressions can be seen, which we label K, L, M, and N. These progressions are more temperature-sensitive than any of those considered above. In so far as these "hot" progressions are developed in the spectrum, they extend by two more intervals of about 600 cm.$^{-1}$, as shown in Fig. 9, the pattern of bands which runs from each C band towards lower frequencies. The extensions join on to the original patterns at the F and J bands. Actually only the patterns associated with the bands $C_1$ and $C_2$ were observed to be thus extended at 200°, but that is doubtless

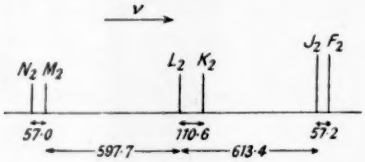



FIG. 9. *Example of the pattern of "hot" bands, an extension of the corresponding main pattern of the acetylene spectrum. (The frequency intervals are between R-heads in cm.$^{-1}$.)*

because the intensity distribution in the spectrum is more favourable for observation of extensions of these two patterns than of the others.

The K and L bands lie about 600 cm.$^{-1}$ on the low-frequency side of the F and J bands. Their separation from each other is exactly the same as that of the E and H bands. The M and N bands lie approximately a further 600 cm.$^{-1}$ towards low frequencies. Their separation from each other is identical with that of the F and J bands, and therefore with that of the B and A bands. Thus, except for the fact that all the periods of about 600 cm.$^{-1}$ are slightly different from each other, the extension of pattern produced by heating is an exact replica of that part of the old pattern which runs from the B and A bands to the F and J bands.

Members have been observed of very weak k and l progressions, displaced 1380 cm.$^{-1}$ above corresponding bands of the K and L progressions.

### (2) Difficulties for the hypothesis of a linear excited state

The assumption that the lower excited states of acetylene are linear, like the ground state, seems so normal that strong reasons are needed for rejecting it. Classified reasons are given below: they are equally the reasons for adopting the particular non-linear model, the consequences of which we shall pursue later.

(a) *General Character of Spectrum.*—Our band-system is essentially a weak system of double-headed bands. We have seen (Fig. 3, p. 2715) that the nearest 2-quantum excited state to which transition from the ground state is allowed is the singlet $\Sigma_u^+$ state, though according to Ross's calculations, it should lie in the far ultra-violet (near 700 Å). Under the hypothesis now considered, our band-system is too weak to be credibly assigned to an allowed electronic transition. The intensity alone might be consistent with the spin-forbidden transition to the triplet $\Sigma_u^+$ state, the calculated position of which, while still in the vacuum region, is much nearer the position of the observed band-system. The difficulty is, however, that the bands are double-headed, therefore having P, Q, and R branches, so that the upper state cannot be a $\Sigma$ state of any kind (eqn. 14, p. 2719).

One could assume an orbitally forbidden transition to one of the lowest singlet states, $\Sigma_u^+$ or $\Delta_u$, supposing that some non-totally symmetrical vibration generates therefrom vibronic states, transitions to which can borrow intensity from allowed electronic transitions further out in the ultra-violet. But there are no vibrations capable of thus producing vibronic states, transitions to which could borrow intensity from the transition to the $\Sigma_u^+$ state (Table 2 and Fig. 4, pp. 2710 and 2715); and even if we could assume some more complicated perturbation so to act, the bands produced would not be double-headed (eqn. 14). The vibration $\Pi_g$ (Fig. 4) would generate vibronic states, transitions to which could borrow intensity from allowed transitions to a $\Pi_u$ electronic state; and the bands produced would be double-headed (eqn. 13, p. 2719). This is a possibility that we can try to entertain, even though none but high-lying $\Pi_u$ electronic states are expected.

(b) *Coarse Structure of the Spectrum.*—The only upper-state vibration which appears in long progressions is that whose frequency in acetylene diminishes from 1049 to 972 cm.$^{-1}$ over the first five quanta. This must be a totally symmetrical vibration (Part III, p. 2717), and, on the hypothesis of linear states, can be nothing else than the C–C stretching vibration of the upper state. The fundamental frequency of the triple bond in the ground

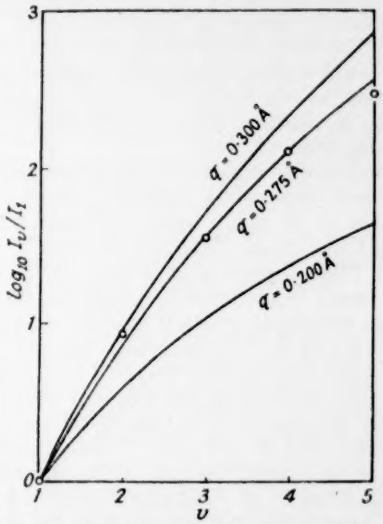



FIG. 10. *Observed intensities of C bands relatively to $C_1$, and calculated relative intensities based on different assumed values* q *of the separation of the origins of the co-ordinates of the vibration in the two electronic states.*

state of acetylene is 1974 cm.$^{-1}$ (Table 9, p. 2716). The fundamental frequency 1049 cm.$^{-1}$ of the upper state suggests a single bond. The C–C bond in the ground state has the length 1·208 Å (Table 16, p. 2720). We can roughly estimate the length of the upper-state C–C bond from the empirical relation, known to hold for different electronic states of a diatomic molecule, namely, $r^2\nu = \text{const.}$ (Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York, 1950, p. 456), if we make the approximation of regarding each CH-group as equivalent to an atom. The result is 1·65 Å.

A somewhat similar result is obtained if we consider the variation of intensity along any of these upper-state progressions, for instance, the strong C progression, transitions to which start from the vibrationless ground state. From $C_1$ to $C_5$ the bands increase in intensity by some 300-fold. This gradient depends (eqns. 9 and 10, p. 2717) on the separation of the origins of co-ordinates of the vibration in the two states; and, by trial, we can find, as is illustrated in Fig. 10, that a separation $q = 0{\cdot}275$ Å reproduces the observed intensity gradient. The difference of bond-length would be $\sqrt{2}$ times this, and hence the upper-state bond has the length 1·60 Å.

On either method of estimation we have in the upper state, supposed linear, a remarkably long C–C bond. This in itself is not a *reductio ad absurdum*; but it will become one when we follow up its consequences for the rotational structure of the bands.

In the meantime, the upper-state progression presents us with another difficulty. On the hypothesis of two linear combining states, the only vibrations which can give progressions are bond-stretching vibrations. Frequencies of about 1000 cm.$^{-1}$ could arise from the stretching of certain types of C–C bond, but are much too low to involve a significant amount of C–H stretching. Since, then, there is little independent hydrogen motion, we have to expect only a small hydrogen-isotope effect on frequency. In fact we find a large hydrogen-isotope effect, the interval of the progression dropping from about 1000 cm.$^{-1}$ in acetylene to about 800 cm.$^{-1}$ in dideuteroacetylene.

A further serious difficulty, one insoluble on the basis of a linear upper state, arises concerning the lower-state progressions, those in about 600 cm.$^{-1}$ in the spectrum of acetylene, and in 500 cm.$^{-1}$ in that of dideuteroacetylene. They are shown to be ground-state progressions by their direction, and by the increasing temperature sensitivity of the successive band-groups, even though some complicating phenomenon, still to be elucidated, is making each such progression one of band-groups, rather than of single bands. The responsible vibration can only be $\Pi_g$ (Table 9, p. 2716). Five successive quanta of this vibration can be seen in the spectrum taken at 200°. It is flatly against the selection rules for vibronic transitions between states of the linear model (Part III, p. 2717) that this non-totally symmetrical vibration should (*a*) appear in long progressions, and (*b*) occur, however weakly, with odd quantum numbers. This is true, even if the whole occurrence of the band-system is due to the presence throughout of one quantum of an upper-state $\Pi_g$ vibration, as was tentatively assumed above: when this quantum is excluded, the total number of quanta in the lower plus upper states of this, as of any, non-totally symmetrical vibration must be even.

The coarse structure of the spectrum presents one other major difficulty for the hypothesis of a linear upper state, namely, that of explaining why most of what would have been expected to be single bands are replaced by groups of bands, groups showing certain regularities, but also differences of form.

(c) *Fine Structure of the Bands.*—Even on the shorter of our two estimates of the C–C bond-length in the linear upper state, 1·60 Å, its moment of inertia must be much larger, and its rotational constant smaller, than those of the ground state, for which the C–C length is 1·21 Å. For acetylene, the rotational constant $B$ must drop from 1·18 cm.$^{-1}$ in the ground state to about 0·7 cm.$^{-1}$ in the excited state. Such a large difference in rotational constants involves the consequence that the R branch of any band will fold back very quickly on itself to form a head. It can be calculated (eqn. 17, p. 2720) that, with $B'' =$ 1·18 cm.$^{-1}$ and $B' =$ 0·7 cm.$^{-1}$, the separation of the R-head from the band origin, which must be very nearly the same as the separation of the R- and the Q-heads, is only 2 cm.$^{-1}$.

The structure of a C band is illustrated in Fig. 11 (facing p. 2727). Here, and throughout the C progression, the separation of the R- from the Q-heads is 17 cm.$^{-1}$. Over all the progressions of double-headed bands, the head-separations lie in the range 13—17 cm.$^{-1}$. In order to provide for such large separations, we need rotational constants of the upper state not much smaller than those of the ground state. Calculation shows (eqn. 17) that, in order to produce the head-separation observed in the C progression, the upper-state value $B' =$ 1·10 cm.$^{-1}$ is required. This in turn leads to a C–C bond-length of 1·27 Å, not much larger than in the ground state, and quite irreconcilable with the lengths deduced from the separations, and from the intensities of the C bands themselves.

The other difficulty presented by the rotational structure is just as serious. It is that the same $B'$ value will not fit the rotational spacing of all three branches of a band. For bands of the C progression, the value $B' =$ 1·10 cm.$^{-1}$ will fit the P and R branches, but the value $B' =$ 1·05 cm.$^{-1}$ is required for the Q branch. This shows that the rotational levels of the excited state are split into doublets, and that transitions giving P and R lines end on the upper, and those giving Q lines on the lower, components of the doublets. On the hypothesis of a linear upper state, we have to interpret this as $K$-type doubling (Part III, p. 2724); but 5% seems an incredibly large difference for which to blame our inability to factorise out the rotational part of the wave function accurately.

Having called attention to Fig. 11, we should note here that the apparent lack of the expected alternation of intensity (Part III, p. 2724) among some of the P and Q lines is

not a difficulty. Among P lines the alternation can be clearly seen only above $J'' = 13$, and among Q lines above $J'' = 18$, although alternation is visible in the R branch up to the unresolved head. The reason, as calculation of the line structure shows, is that, throughout the lower values of $J''$, the strong ($J''$ odd) P lines almost coincide with the weak ($J''$ even) Q lines, and the weak P lines with the strong Q lines, though the two series gradually separate until, for higher $J''$ values, they are fully resolved.

### (3) Analysis on the basis of a *trans*-bent excited state

(a) *General Picture of the Lower-state Progressions.*—All the difficulties discussed in preceding Sections are removed if we assume a planar *trans*-bent excited state. We choose the *trans*-bent, rather than the *cis*-bent planar state for continued consideration, because the former offers an obvious hope, which the latter does not, of accounting for the progressions towards decreasing frequencies in intervals of about 600 cm.$^{-1}$ in acetylene and 500 cm.$^{-1}$ in dideuteroacetylene. It is included in this hope that we can supply adequate interpretations of the rather complicated variations in the precise intervals, and of the appearance at each step of band-groups instead of single bands; but we leave aside these points for the moment. Naturally, a correct analysis will give a good account also of the upper-state progressions, and of the peculiar fine-structures of the bands.

The only vibration of normal acetylene, whose frequencies are even roughly of such magnitude that it might conceivably be made responsible for the observed lower-state progressions, is the *trans*-bending vibration $\Pi_g$, the fundamental frequencies of which are 613 cm.$^{-1}$ in acetylene and 511 cm.$^{-1}$ in dideuteroacetylene. The only kind of acetylene model with respect to which this vibration is totally symmetrical is the *trans*-bent model ($C_{2h}$). The first essential condition for a vibration to produce progressions is that it should be totally symmetrical with respect to the *common* symmetry of the combining models; and the common symmetry of the straight and bent models is the same as the symmetry of the bent model. The two $\Sigma_g^+$ stretching vibrations and the $\Pi_g$ bending vibration of the linear model correlate with the three totally symmetrical vibrations of the *trans*-bent model, and thus all three vibrations of either state are qualified by their symmetry to appear without restriction as to quantum number (Fig. 4, p. 2715).

But if the transition is from a lower linear to an upper *trans*-bent state, then on the general grounds of the Franck–Condon principle, we should expect the $\Pi_g$ vibration to generate the really important lower-state progressions. For this, more than any other, is the vibration which, before excitation, can deform the molecule towards the shape in which it has to live after excitation. Up to a point, each previously present quantum of this vibration must increase the transition probability. And so we can understand why, in spite of most forbidding Boltzmann factors, up to five quanta can be seen, a most unusual occurrence for lower-state progressions in absorption spectra. Thus, from any C band, the first lower-state quantum leads to the A and B bands, which at 20° are each about one-third of the strength of the C band, although if the transition probability did not alter, their Boltzmann factors would make each one-twentieth of the strength of the C band. The effect of the moderated intensity ratio on the observable length of the progression is evident.

The two $\Sigma_g^+$ vibrations have fundamental frequencies so much larger than that of the $\Pi_g$ vibration (Table 9, p. 2716), and therefore Boltzmann factors so much smaller ($10^{-4}$ to $10^{-7}$ at 20°), that we should not expect them to generate observable lower-state progressions, especially as they cannot produce counteracting increases of transition probability comparable to those given by the $\Pi_g$ vibration.

(b) *General Picture of Upper-state Progressions.*—Under the hypothesis of a *trans*-bent excited state, symmetry laws will allow upper-state progressions to be generated by any of the totally symmetrical vibrations of the upper state, that is, any from among the two stretching vibrations, $A_g$(C) and $A_g$(H), and the bending vibration, $A_g(\alpha)$, which correlate respectively with the stretching vibrations $\Sigma_g^+$(C) and $\Sigma_g^+$(H), and the bending vibration $\Pi_g$, of the linear state (Fig. 4, p. 2715). However, on the basis of the Franck–Condon principle, we expect the long and dominant progressions, those about 1000 cm.$^{-1}$ in acetylene, and about 800 cm.$^{-1}$ in dideuteroacetylene, to be generated by the bending vibration $A_g(\alpha)$. This is the vibration which, more than any other, must be produced up to large classical

amplitudes in consequence of excitation from a linear ground state to a *trans*-bent excited state. As Boltzmann factors do not enter into intensity relations in an upper-state progression, we can understand why successive bands in these progressions get continually and markedly stronger towards higher frequencies. The large increase in C–C length, which on the hypothesis of a linear upper state was required to explain this strengthening along upper-state progressions, is here replaced by the large change in the CCH angles.

We have no difficulty now in reconciling the magnitude of the frequencies of the upper-state vibration with their isotopic separation. For 1000 cm.$^{-1}$ is an entirely normal value for a CCH bending frequency, and, since most of the motion is in the hydrogen atoms, a large hydrogen-isotope shift is to be expected.

On this basis we can understand the greater weakness of the progressions of dideutero-acetylene at the low-frequency end of the spectrum, and also their smaller increase in intensity along the spectrum, towards higher frequencies, as compared with the progressions of acetylene. The CCD bending vibration will have a smaller classical amplitude than the CCH vibration: quantally, the oscillator wave-function of the former will be the more compact. It follows that upper- and lower-state vibronic wave functions will overlap less at low quantum numbers, and that the increase in overlap with increasing quantum number will be less, for $C_2D_2$ than for $C_2H_2$. This, according to the Franck–Condon principle, will produce just those intensity relations which have been described.

Since Boltzmann factors do not inhibit the appearance of upper-state frequencies, one might expect to find those of the totally symmetrical stretching vibrations $A_g$(C) and $A_g$(H), though only in relatively weak and short progressions, because these vibrations are much less important for the mutual accommodation of the combining models. The interpretation which we shall offer of the many weak series of bands, those labelled with lower-case letters, is that they represent the first steps of progressions in these upper-state stretching vibrations.

(c) *Development of Band Groups in Lower-state Progressions.*—A simplified statement can be made about the observed structure of lower-state progressions, if at first we neglect the weak bands D and G, which will be considered separately later. Then, each progression originates with a single band, C, but continues with band pairs: B, A; H, E; F, J; K, L; M, N. The separations between the bands of the pairs are alternately narrow and wide, the two spacings, one just half the other, being precisely repeated along any one lower-state progression. The intervals between the pairs are near 600 cm.$^{-1}$ in the acetylene spectrum, and the spacings are near 60 and 120 cm.$^{-1}$, but increase somewhat as we pass from one lower-state progression to the successive replicas of it which are encountered on ascending upper-state progressions. In the spectrum of dideuteroacetylene the gaps between the pairs are about 500 cm.$^{-1}$, and the two pair-spacings are about 40 cm.$^{-1}$ and 80 cm.$^{-1}$.

The hypothesis of the bent upper state explains all this. The bent state is an asymmetric top with three different rotational constants $A$, $B$, and $C$. Without troubling yet about precise figures, let us consider their orders of magnitude. Supposing that the bending is moderate, say 30° or 60°, then, because of the mass ratio of carbon and hydrogen, $A$ will be one order of magnitude larger than $B$ and $C$, which will both be comparable to the $B$ of normal acetylene, and thus of the order of 1 cm.$^{-1}$ (Table 16, p. 2720). Hence $A$ must be of the order of 10 cm.$^{-1}$. Furthermore, because of the relation between moments of inertia in a planar molecule, the reciprocals of $B$ and $C$ will differ approximately by the reciprocal of $A$, so that $B$ and $C$ should show a difference of the order of 0·1 cm.$^{-1}$. It is the magnitude of $A$ which will concern us first.

Since the bent upper state is a near-symmetric top, its rotational energy will approximately obey eqn. 18 (p. 2720). It follows that the manifold of energy levels will contain a system of large spacings dependent upon $K$: as $K$ takes on the values 0, 1, 2, 3, . . ., so the energy is increased by 0, 1, 4, 9, . . ., units $\{A - \frac{1}{2}(B + C)\}$, each unit of the order of 10 cm.$^{-1}$. Therefore, when, as in the upper part of Fig. 12, we sort out the energy levels into a series of gyrovibronic stacks, distinguished with respect to $K$, the stacks will start successively higher by 1, 4, 9, . . ., units $\{A - \frac{1}{2}(B + C)\}$ above the starting point of the lowest stack.

As eqn. 15 shows (p. 2719), there are two possible selection rules for $K$, depending on the direction of the oscillating transition moment, which in turn depends on the symmetry, still to be discussed, of electronic orbital motion in the excited state: if the oscillating moment is parallel to $a$, then $\Delta K = 0$; but if perpendicular, then $\Delta K = \pm 1$. The second of these rules is required to explain our band pattern.

When transitions start from the vibrationless ground state, a $\Sigma_g^+$ vibronic state for which $K'' = 0$, then they have to end in the upper gyrovibronic state for which $K' = 1$; and thus we obtain the single band C, which heads the progression.

When transitions start from the next higher vibronic state, the $\Pi_g$ state, which has one quantum of the $\Pi_g$ vibration, with its unit of angular momentum, so that $K'' = 1$, they may end either in the upper gyrovibronic state for which $K' = 0$, or in that for which $K' = 2$. The former alternative gives band A, whose separation from band C is equal to the lower-state vibration quantum plus one of the upper-state gyrovibronic spacing units: $\Pi_g(1) + \{A - \frac{1}{2}(B + C)\}$. The latter alternative leads to band B, whose separation from C is the vibration quantum less three of these spacing units: $\Pi_g(1) - 3\{A - \frac{1}{2}(B + C)\}$. Thus the B − A spacing is $4\{A - \frac{1}{2}(B + C)\}$—roughly 60 cm.$^{-1}$ in acetylene, or 40 cm.$^{-1}$ in dideuteroacetylene, according to observation.

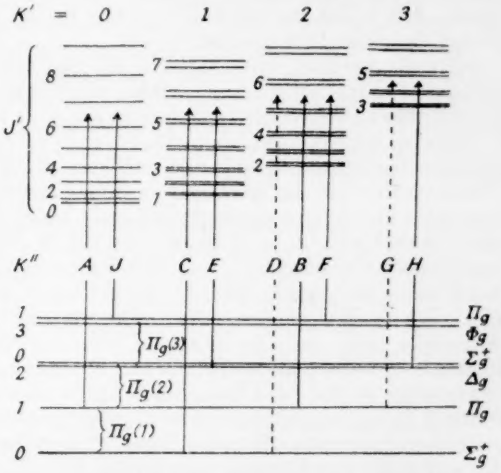



FIG. 12. *Gyrovibronic transitions obeying the rule* $\Delta K = \pm 1$ *(full-line arrows) to* trans*-bent upper state: explanation of band groups in the lower-state progressions. The long horizontal lines each mean one vibronic state, but the whole of the upper part of the diagram represents a single vibronic state dissected into its gyrovibronic states, and their levels and sub-levels. (Two forbidden transitions are marked by broken-line arrows.)*

With two $\Pi_g$ vibration quanta initially present, the vibronic $\Delta_g$ state, for which $K'' = 2$, can combine with upper gyrovibronic states for which $K' = 1$ and 3. The former transitions produce band E, separated from C by the two $\Pi_g$ quanta only: $\Pi_g(1) + \Pi_g(2)$. The latter transitions give band H, separated from C by the two vibration quanta less eight gyrovibronic spacing units: $\Pi_g(1) + \Pi_g(2) - 8\{A - \frac{1}{2}(B + C)\}$. Thus the H − E spacing is $8\{A - \frac{1}{2}(B + C)\}$—about 120 cm. in acetylene and 80 cm.$^{-1}$ in dideuteroacetylene, that is, twice the B − A spacing.

The whole of this can be followed from Fig. 12, the upper part of which represents the detail of one upper vibronic state, and is on a much more open scale than the lower part, which comprises, but without detail, a series of lower vibronic states. When the lower electronic state is furnished with successive $\Pi_g$ quanta, each of which may either add its unit of angular momentum to, or subtract it from, the total of the units already present, groups of vibronic states arise which alternately contain all even and all odd numbers of units of angular momentum. Thus in the successive groups of lower vibronic states, $K''$ takes on the following values: 0; 1; 0, 2; 1, 3; 0, 2, 4; 1, 3, 5; . . . The states of a given group are separated in energy on account only of the anharmonicity of the $\Pi_g$ vibration. According as $K''$ is 0, or 1, or 2, we get respectively, the single band, such as C, the closer type of band pair, such as B, A, and F, J, and M, N, or the doubly spaced type of band pair, such as H, E, and K, L.

A number of bands are allowed by the $K$ selection rule which are not observed, namely, those of the initial vibronic states for which $K'' = 0$ in the two- and four-quantum groups, and those of initial vibronic states for which $K'' = 3$ or more. The missing bands of the states having $K'' = 0$ should be nearly coincident with, and may possibly be obscured under, bands E and L. Bands involving high $K$'s should be well separated from other bands in some cases; but they are expected to be weak, and presumably are too weak to be observed.

(d) *Symmetry of the Upper Electronic State.*—We have mentioned three features of the spectrum, which provide more than enough evidence to determine the symmetry of orbital motion in the excited electronic state. By dealing with this point now, we can shorten the more quantitative discussions of band forms given later.

First, it was noted (Section I, p. 2726) that nearly all the bands, in fact all that can be clearly observed except the D bands, are double-headed. It follows by relations (13), (14), and (8) (pp. 2719 and 2716) that the electronic oscillations of the transition are perpendicular to axis $a$. It then follows from Table 8 (p. 2712) and Fig. 3 (p. 2715) that the oscillations of the transitions are almost certainly parallel to axis $c$, since if they were perpendicular to $c$ we should find strong bands indicating electronic oscillations both parallel and perpendicular to $a$. The conclusion is that the upper state has $A_u$ symmetry, that is, that it has the two-fold $c$ axis of the bent model, but changes sign on reflexion through the plane of the atoms.

Secondly, we have found (Section 3c) that the selection rule $\Delta K = \pm 1$ is required to explain the characteristic band pattern of the spectrum. This leads directly to relations (8), and thus to the chain of conclusions stated in the last paragraph.

Thirdly, we have the approximate analysis of C bands already described. As the experiments on the temperature dependence of band intensity show, the transitions giving C bands start from the vibrationless ground state; and, by the selection rule $\Delta K = \pm 1$, they must end in the upper gyrovibronic states for which $K' = 1$. As Fig. 12 shows, each $J'$ value here, as in all upper gyrovibronic states for which $K' > 0$, is theoretically to be represented by a doublet, because the excited molecule is only a near-symmetric top, so that $B$ and $C$ are slightly different, the difference being of the order of 0·1 cm.$^{-1}$, as we have seen. We noted in Section 2c (p. 2730), that the rotational structure of C bands makes it empirically clear, not only that the upper rotational levels are in fact double, with a difference of rotational constant of this order of magnitude, but also that the principle of construction of the band branches is that Q-branch transitions end on the lower, while P- and R-branch transitions end on the upper sub-levels of the doublets. If now we recall the overall selection rules (20) and (21) (pp. 2722, 2723), and consult Fig. 5 (p. 2721), we see that the only upper gyrovibronic state having $K' = 1$, with which the lower vibronic state $\Sigma_g^+$ (col. 1) could combine to give bands formed according to this principle, is the gyrovibronic state $A_u$ (col. 8). As the only vibrations which may be present are totally symmetrical, this means that the electronic state has $A_u$ symmetry.

(e) *Rotational Structure of C Bands.*—Our next task is to deal with the structure of the C bands quantitatively, and thus to determine the three rotational constants $A$, $B$, and $C$ of the excited molecule. The broad relation between the structure and the constants is that the doublet splitting depends on the difference between $B$ and $C$, and, because of the approximate reciprocal relation already mentioned, on $A$, while the $J$ spacings depend essentially on the magnitudes of $B$ and $C$ themselves. The displacement of the whole gyrovibronic band from the vibronic origin depends mainly, as we have noted, on $A$, and thus indirectly on the difference between $B$ and $C$.

By using the exact equation for the energy of an asymmetric top (eqn. 19, p. 2720), and the associated tables of King, Hainar, and Cross, it is possible, by trial and error, to find values of the three rotational constants of the excited acetylene molecule, which give calculated positions for the rotational lines in good agreement with the measured positions. These calculations have been carried through for the four bands $C_0$—$C_3$, and, for illustration, the results of one such calculation, and their comparison with the observational data are given in Part V (following paper). Here we direct attention to the rotational constants thus derived, which are assembled in Table 17. The quantities $\{A - \frac{1}{2}(B + C)\}$

are also listed for comparison with values obtained from the separations of band pairs, and recorded below.

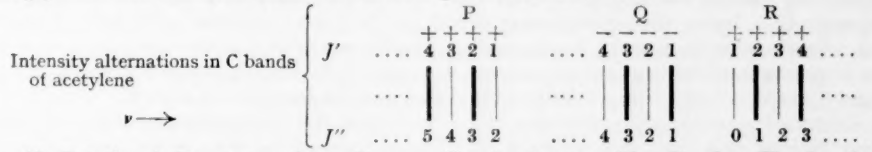
TABLE 17. *Rotational constants (cm.$^{-1}$) of the* trans-*bent state of acetylene from the analysis of C bands* ($C_v$).

| $v$ | $A$ | $B$ | $C$ | $A - \frac{1}{2}(B + C)$ |
|---|---|---|---|---|
| 0 | 12·50 | 1·125 | 1·032 | 11·42 |
| 1 | 13·80 | 1·126 | 1·030 | 12·72 |
| 2 | 15·10 | 1·123 | 1·025 | 14·03 |
| 3 | 16·36 | 1·123 | 1·025 | 15·29 |

In Table 17, $v$ represents the number of quanta of the $A_g(\alpha)$ vibration (Fig. 4, p. 2715) in the upper vibronic state. That $A$ increases markedly with the energy of this vibration is consistent with our picture of the geometry of the excited molecule and of this vibration. Without troubling about a mathematical proof, one can see this intuitively by thinking of a classical $A_g(\alpha)$ vibration of such large amplitude that the separation of the mass-points from axis $a$ alternately becomes double the equilibrium separation, and zero: then the instantaneous $A$ will vary between a quarter of its equilibrium value and infinity, so that its average value is infinite.

These calculations confirm such assignments of $J$ values to observed lines as are illustrated in Fig. 11 (facing p. 2727): the assignments are uniquely determined by the necessity of obtaining the correct doublet splitting simultaneously with the correct $J$ spacing. The calculations and assignments confirm the assumption of coincidences, too close for resolution with our equipment, between odd-numbered P lines and even-numbered Q lines, and between even-numbered P lines and odd-numbered Q lines, over the first 12 lines of the P branch, an assumption that we have to make for the independent reason that only thus can we account for the apparent absence of intensity alternations in this range, despite its evident presence elsewhere in the bands.

The assignments also bring about agreement between observation and theory as to the precise pattern of the alternations in the C bands. The theory can be deduced from Fig. 5 (p. 2721), remembering that the $a$ levels have the higher statistical weight in acetylene. The pattern is shown in the following diagram, in which upper and lower members of doublet levels in the electronic upper state are distinguished by + and − signs, respectively. Lower-state $J''$ values being used, as always, to number the lines, the rule for C bands is simply that odd-*numbered* lines are the stronger in all three branches:




(f) *Rotational Structures of the Stronger Temperature-sensitive Bands.*—The bands A and B have a common vibronic origin which lies lower than that of the bands C by the fundamental vibration $\Pi_g$ of the electronic ground state. The distinction between the bands A and B, both as to position and structure, is gyrovibronic. The A-band transitions end in the upper gyrovibronic state for which $K' = 0$. Hence the gyrovibronic origins of bands A are identical with their vibronic origins; and hence also all the upper-state energy levels are single. The B-band transitions end in the upper gyrovibronic state for which $K' = 2$. Therefore the gyrovibronic origin of bands B will lie higher; and also all the upper-state levels will be double. However, since the transitions start from degenerate $\Pi_g$ levels, transitions from each such level will end on both members of the upper-state doublets involved; and hence all lines of all branches of bands B will be double.

Having deduced our rotational constants from the C bands, we can use them to calculate, again using eqn. 19 and the tables of King, Hainar, and Cross, the positions relatively to their vibronic origin, of the gyrovibronic origins, and of the individual lines, of the A and B bands. These calculations have been made for the bands $A_1$, $A_2$, $A_3$, $B_1$, $B_2$, and $B_3$, of acetylene, and the detailed results for the lines of one A band and one B band are reported in Part V, where they are compared with the experimental measurements.

As can be followed with the aid of Fig. 5 (p. 2721), intensity alternations should theoretically appear in the A bands; and they can be seen, except when masked by lack of resolution near band heads, or by overlap of lines of the P and Q branches. The pattern of the alternations is slightly different from that of C bands : for acetylene it is that odd-numbered lines of Q branches, and even-numbered lines of P and R branches, are stronger than the intervening lines. Theoretically, the doublets of the B bands should have a strong and a weak component, which change sides as we pass from one doublet to the next along a branch. Experimentally, the lines of the B bands appear somewhat diffuse and without alternation of intensity : the reason is that our photographs do not resolve the doublets, though we do see the shelving intensity due to their weaker components.

The bands E and H have a common vibronic origin, lying below that of the bands A and B by another quantum of the $\Pi_g$ vibration. The transitions giving the bands E and H end in the upper gyrovibronic states for which $K' = 1$ and 3, respectively. The positions of the gyrovibronic origins, and of the individual lines, relatively to the vibronic origin, have been calculated for some of the bands. The results of such calculations are indicated by some line assignments given in Part V.

Theoretically, the lines of E and H bands are doublets, each with a strong and a weak component, just like the lines of the B bands. Experimentally, we observe with E and H bands, as with B bands, a series of somewhat diffuse lines, representing unresolved doublets, and showing no alternation of intensity. This is how we know that the transitions giving the E bands start from the vibronic state $\Delta_g$, and not from the neighbouring 2-quantum state $\Sigma_g^+$ : if they started from the $\Sigma_g^+$ state, the E bands would show intensity alternations like C bands.

The bands J and F have another common vibronic origin displaced by a further $\Pi_g$ quantum below that of the E and H bands. In separation and structure, these bands are simply weaker replicas of the A and B bands, respectively. This shows that the transitions giving the bands end in upper gyrovibronic states for which $K' = 0$ and 2 respectively, and therefore must commence in the 3-quantum vibronic state $\Pi_g$ for which $K'' = 1$. Some assignments based on calculated line positions are given in Part V.

The " hot " bands were observed too weakly to permit an extensive examination of their rotational structures. However, the separation of the K and L bands, identical with that of the H and E bands, makes it almost certain that the transitions start in the 4-quantum vibronic state $\Delta_g$, and end in upper gyrovibronic states for which $K' = 3$ and 1, respectively. Again, the separation of the M and N bands, identical with that of the B and A bands, and the F and J bands, makes it highly probable that the transitions start in the 5-quantum vibronic state $\Pi_g$ and end in upper gyrovibronic states for which $K' = 2$ and 0, respectively. Some calculated line assignments are given in Part V.

Comment is necessary concerning the accuracy of the calculations of line positions. King, Hainar, and Cross give tables of $E(\kappa)$ for $\kappa$ values spaced 0·1 apart; they also give methods of interpolation for intermediate values of $\kappa$. Our $\kappa$'s lie about 0·014—0·017 within one end of the range of $\kappa$, and we obtained the corresponding $E(\kappa)$'s by three-point graphical interpolation. This method of calculation is not as accurate as some of the experimental measurements would warrant. The alternative would have been to use the above-named authors' methods of numerical interpolation. However they are so difficult in this particular application that the labour seemed unjustified. With the rapid methods used, we could deduce the rotational constants, and, for C bands, calculate the positions of the lines to about the accuracy of measurement. For other bands, we could compute the gyrovibronic-origin and the band-head separations with almost the same accuracy, though the calculated line positions were not always as good as the measured positions.

The gyrovibronic-origin separations of the band pairs give a useful check on the rotational constants, since, by division by 4 or 8, they afford independent and fairly accurate estimates of the quantity $\{A - \frac{1}{2}(B + C)\}$. These values are given in Table 18. For acetylene, the origin separation is taken as the observed Q-head separation. For dideuteroacetylene, owing to incomplete resolution, the Q heads were somewhat poorly defined and therefore we thought it better in this case to use the experimentally well-defined R heads.

(g) *The Forbidden Progressions* D *and* G.—The D bands are weak satellites on the high-frequency side of the C bands, and the G bands are still weaker satellites on the same side of the B bands. We assign the D bands, which are not weakened by cooling, to transitions from the vibrationless ground state $\Sigma_g^+$ for which $K'' = 0$, to the upper gyrovibronic state for which $K' = 2$, and the G bands, which are temperature sensitive, to transitions from the lowest $\Pi_g$ vibronic state, for which $K'' = 1$, to the upper gyrovibronic state for which $K' = 3$ (Fig. 12, p. 2733). In both cases $\Delta K = 2$, in contravention of the $K$ selection rules of the symmetric top (eqn. 15, p. 2719).

TABLE 18. *Values of* $\{A - \frac{1}{2}(B + C)\}$ *in cm.*$^{-1}$ *from band-pair separations.*

| | | $C_2H_2$ (from Q heads) | | | $C_2D_2$ (from R heads) | | |
|---|---|---|---|---|---|---|---|
| Band-pair | | B − A | H − E | F − J | B − A | H − E | F − J |
| $v$ | 1 | 12·70 | 12·80 | 12·70 | — | — | — |
| | 2 | 14·17 | 14·04 | 14·00 | 8·52 | — | 8·45 |
| | 3 | 15·45 | 15·35 | — | 9·12 | 8·92 | 9·05 |
| | 4 | 16·72 | 16·39 | — | 9·72 | 9·38 | 9·65 |
| | 5 | — | 16·86 | — | 10·10 | 9·86 | 10·02 |
| | 6 | — | — | — | 10·20 | — | — |

The strongest evidence for our assignment of these bands relates to their positions. This is so consistent among lower-state progressions differing with respect to the number of upper-state vibrational quanta, all of which have slightly different energies, that one cannot doubt that the bands really belong to the gyrovibronic patterns into which the lower-state progressions are elaborated by the asymmetric-top character of the upper state. The best defined points for measurement in these weak bands are their R heads, the positions of which we can calculate to within about 1 cm.$^{-1}$ of the observed intensity maxima, from our rotational constants.

The forms of the bands are interesting, although, owing to low intensities, they could not be studied in detail. However, the D bands are certainly single-headed, presumably having no Q branch: they constitute, indeed, the only obvious series of single-headed bands in the spectrum. Some at least of the G bands appear to be double-headed, but with a peculiarly narrow spacing, about 2·5 cm.$^{-1}$, between the intensity maxima: it seems that these bands have Q branches.

If we were dealing with symmetric-top states only, we would be tempted to diagnose (eqns. 13 and 14, p. 2719) transitions, which, when they start from a $\Sigma_g^+$ vibronic state give bands without Q branches, but when they originate in a $\Pi_g$ state produce bands with Q branches, as following those $J$ selection rules which apply when $\Delta K = 0$, and therefore as involving electronic oscillations parallel to axis $a$ (eqn. 15, p. 2719). We are actually dealing with an asymmetric top, which the concept of $K$ is extended to cover, even though it can be numerically defined therefor only by the limit into which it goes when the top becomes symmetric. Thus, in our case, the $K$ rules of the symmetric top are not expected to hold strictly; and, in particular, the conditions for transitions with electric oscillations parallel to $a$ are broader than is indicated above. If both upper and lower states are regarded as asymmetric tops, general or limiting, then either a rotational state of top-species $A$ must combine with one $B_a$, or a rotational state $B_b$ must combine with one $B_c$ (eqn. 16, p. 2719). As one of our states belongs to the limiting case of no asymmetry, a more specific expression of the condition is that a $\Sigma$ rotational state of the linear molecule must combine with either an $A$ or a $B_a$ state of the bent molecule, whilst a $\Pi$ linear state must combine with either a $B_b$ or a $B_c$ bent state (Table 15, p. 2720). These combinations are permitted when $\Delta K$ is even, and, in particular, when $\Delta K = 2$ (Fig. 5, p. 2721). It can also be argued, conversely, that transitions with $\Delta K = 2$ must involve electronic oscillations parallel to $a$.

The conclusion that the forbidden ($\Delta K = 2$) bands D and G have their electric oscillations of transition parallel to $a$, whereas all the allowed ($\Delta K = \pm 1$) bands have their oscillations parallel to $c$, is consistent with the observation that the forms of the D and G bands are strikingly different from those of all the other bands. Regrettably, we cannot analyse the differences in a more detailed way, for lack of sufficiently strong photographs.

What is forbidden about these bands is not that $\Delta K = 2$, a difference allowed to an asymmetric top, but that the overall selection rules, which must be obeyed in all circumstances (eqns. 20 and 21, pp. 2722, 2723), and the asymmetric-top rules mentioned above,* are not simultaneously satisfied for combinations of the lower vibronic states with the relevant vibronic states of an upper electronic state $A_u$ (Fig. 5, p. 2721). Yet the band-systems to which the D and G bands are shown by their positions to belong, certainly depend on transitions to vibronic states of an electronic state $A_u$ (Section 3d, p. 2734). However, the asymmetric-top and the overall selection rules would be obeyed, with $\Delta K = 2$, if the upper electronic state were of species $B_u$ (Fig. 5). We conclude that some perturbation is mixing a small amount of $B_u$ character with the $A_u$ electronic state of the *trans*-bent acetylene molecule.

A conceivable electronic state from which the $B_u$ character might be borrowed is suggested by our correlation diagram (Fig. 3, p. 2715). Our upper electronic state $A_u$ is clearly to be identified with the lower of the two $A_u$ states represented on the left of the diagram. Transitions from the electronic ground state to this state are allowed only in consequence of *trans*-bending, but become forbidden as the molecule is straightened (and remain forbidden with *cis*-bending). The energy curve of this state is seen to be intersected, at a certain degree of *trans*-bending, by the much steeper curve of a $B_u$ electronic state, to which transition from the electronic ground state is allowed, not only in all bent configurations, but also in the limit of no bending, when the energy is very much higher. The ultra-violet spectrum of this upper state might well be a continuum, the energy curve being more a wall than a hollow; but as the energy must neighbour that of the $A_u$ state over a range of the configurations through which the molecule must pass during excitation from the electronic ground state, some electronic resonance between the two states seems possible, provided that a suitable mixing perturbation can be found. As noted already (Section 1b, p. 2726), the presence of a continuous spectrum underlying our band spectrum is not excluded by our observations.

The mixing potential has to have $B_g$ symmetry (Table 4, p. 2711). The condition that it must make no noticeable difference to band positions, excludes a vibration; and anyway, no single vibration has $B_g$ symmetry (Fig. 4, p. 2715). It could be a rotation, since, for all we know, line positions in the B and G bands may be displaced; and rotation round axis *a* has $B_g$ symmetry. Though we cannot prove it, this seems the best speculation at present. We are attracted to it by the knowledge that molecular rotation round *a*, and electronic orbital motion, must be coupled together by the yoke they share as common carriers of the angular momentum in straight-to-bent transitions. The coupling energy could be due to Coriolis forces.

In the spectrum of dideuteroacetylene the D bands cannot be seen, probably because they are obscured by the q and p bands which overlap each C band.

(h) *The Minor Progressions.*—Corresponding to the main progressions, A, B, C, . . ., we find, shifted to higher frequencies in the spectra of acetylene and dideuteroacetylene, much weaker progressions, labelled a, b, c, . . ., respectively; and, shifted to still higher frequencies in the spectrum of dideuteroacetylene, a further series of not quite such weak progressions, which we label p, q, r, . . ., respectively. The progressions a, b, c, . . ., are weaker relatively to the main progressions in the spectrum of acetylene than in that of dideuteroacetylene. In the spectrum of acetylene the progressions p, q, r, . . ., could not be found. In the spectrum of dideuteroacetylene, the positions of the bands, which, if observed, we would have labelled h, are covered by the stronger observed bands t. The correspondences are indicated in the following scheme:

| Main progns. ..... | | A | B | C | E | F | H | J | K | L | Approx. shift (cm.$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Minor progns. | $C_2H_2$ | a | b | c | e | f | h | j | k | l | + 1380 |
| | $C_2D_2$ | a | b | c | e | f | — | j | — | — | + 1300 |
| | $C_2D_2$ | p | q | r | t | u | w | y | — | — | + 2200 |

In any vertical column of this scheme, the progressions show the same sort of dependence of intensity on temperature: progressions c and r are not weakened by cooling, whilst

* Asymmetric-top rules should not be broken by a symmetric top, which is only a limiting case.

a, b, p, and q are weakened, e, h, t, and w are weakened more, and f, j, u, and y more still. Thus it is clear that the common frequency shift applying to each horizontal row in the above scheme represents a vibration frequency of the upper electronic state.

As we are dealing throughout, not with single bands, but with progressions, in intervals of about 1000 cm.$^{-1}$ in acetylene and about 800 cm.$^{-1}$ in dideuteroacetylene, there might have been some dubiety concerning the frequency shifts entered to the right of the above scheme of progressions. However, we can be sure that the first figure should indeed be 1380 cm.$^{-1}$, and not 380 cm.$^{-1}$ or 2380 cm.$^{-1}$, because, in the acetylene spectrum, we can find the first bands, $a_0$, $b_0$, $c_0$, . . ., of the minor progressions, as well as those $A_0$, $B_0$, $C_0$, . . ., of the major ones. Although we cannot do this in the spectrum of dideuteroacetylene, because of the small intensities at low quantum numbers, we have deduced the origin of the band system (next section), and therefore the correlation, as between acetylene and dideuteroacetylene, of the origins and band quantum-numbers. Thus, the analogies between the spectra point, with a high degree of probability, to the conclusion that the relevant dideuteroacetylene shift is about 1300 cm.$^{-1}$, as entered above, and is not more or less than this by the progression interval 800 cm.$^{-1}$. No such correspondence between the spectra helps us to define the frequency of dideuteroacetylene relevant to the progressions, p, q, r, . . ., the observed bands of which would allow it to be taken near 600 cm.$^{-1}$, or near 1400 cm.$^{-1}$, or near 2200 cm.$^{-1}$. However, we can account satisfactorily for the appearance of these progressions in the spectrum of dideuteroacetylene only on the basis that the common shift which characterises them is near 2200 cm.$^{-1}$, as is noted above.

After the totally symmetrical bending vibration $A_g(\alpha)$, the two vibrations of the upper state which should appear most strongly in these spectra are the two totally symmetrical stretching vibrations $A_g$(C) and $A_g$(H). Even harmonics of non-totally symmetrical vibrations are symmetry-allowed, but should appear much more weakly, if at all. We assign the approximate frequencies, 1380 cm.$^{-1}$ in acetylene and 1300 cm.$^{-1}$ in dideuteroacetylene, to the upper-state carbon-bond-stretching vibration $A_g$(C). The isotopic difference of frequency is consistent with assignment to a carbon vibration. On the Franck–Condon principle, progressions in successive quanta of vibration $A_g$(C) cannot be expected to increase in intensity with increasing quantum number at a rate comparable to that of progressions in the $A_g(\alpha)$ vibration. And thus, as we proceed towards higher frequencies, progressions in the $A_g$(C) vibration will soon get lost beneath the rapidly strengthening bands of the $A_g(\alpha)$ progressions. Thus we account for the fact that we have not been able to observe a second quantum of the $A_g$(C) vibration.

The approximate frequency 2200 cm.$^{-1}$ of dideuteroacetylene is attributed to the hydrogen-stretching vibration $A_g$(H). This is a form of motion, which, in the bent molecule, is bound to be accompanied by small angular changes, which would not much reduce the frequency, but would lend the vibration an appreciable intensity in the spectrum. In acetylene the smaller hydrogen masses would lead to less bending and smaller intensities; but we think that the main reason why we do not observe the system of minor progressions, p, q, r, . . ., in the spectrum of acetylene is that their displacement from the main progressions would, according to our assignment of the responsible vibration, be about 3000 cm.$^{-1}$, so that each band of any such minor progression would approximately agree in position with a very much stronger band of main progression, a band having three extra quanta of the intensifying vibration $A_g(\alpha)$. In fact, we observe in a number of the main bands, $C_4$ and $C_5$ for instance, disturbances to the rotational structure, or to the whole band position, which suggest a Fermi effect following accidental coincidences of upper vibronic states of like symmetry. By an examination of such perturbations in the C progression, we have arrived at the opinion that the fundamental frequency of the $A_g$(H) vibration in $C_2H_2$ is indeed close to 3000 cm.$^{-1}$. We do not find a second quantum of this vibration, either in the spectrum of acetylene or in that of dideuteroacetylene. The reason why we should not expect to do so is as given in the preceding paragraph, but is still more cogent in its application to this case, since higher frequencies are involved.

(i) *Origin of the Band-system.*—In the spectrum of acetylene, no member of the C progression has been found at lower frequencies than that of the band labelled $C_0$. Its

R-head is at 42,225·5 cm.$^{-1}$, and its gyrovibronic origin is calculated from the rotational analysis to be at 42,209·1 cm.$^{-1}$. No member of the heat-strengthened progressions A and B has been observed on the low-frequency side of the bands labelled $A_0$ and $B_0$. Bands of the weaker progressions E and H have been found down to $E_0$ and $H_0$ near 41,000 cm.$^{-1}$, and various other weak bands are recorded down to 40,500 cm.$^{-1}$. Thus it seems certain that $C_0$ is really the first band of the C progression, and therefore that the quantum numbers indicated by subscripts in the labels of all the acetylene bands have been correctly assigned.

A small part of the energy at the gyrovibronic origin of the band $C_0$ is due to the one *K*-unit of rotation in the upper state (Fig. 12, p. 2733). Correcting for this by deduction of the appropriate value of $\{A - \frac{1}{2}(B + C)\}$, we find (Table 17, p. 2735) for the vibronic origin of $C_0$, which is also the electronic origin of the whole band-system of acetylene, the value 42,197·7 cm.$^{-1}$.

The spectrum of dideuteroacetylene presents the difficulty that, owing to its small intensity at the low-frequency end, we could not observe the early members of the progressions. On the assumption, for the moment, that we have assigned quantum numbers correctly to the observed bands, the situation with respect to the C progression is that bands $C_1$ and $C_0$ have not been observed; however, we can deduce their positions very approximately by extrapolation from the observed positions of the bands $C_6$ to $C_2$. This leads us to expect $C_1$ at 43,124 cm.$^{-1}$ and $C_0$ at 42,280 cm.$^{-1}$. These extrapolated figures, like the observations from which they are derived, refer to R-heads. According to calculations based on rotational constants of dideuteroacetylene given later, the band origins should lie 13 cm.$^{-1}$ lower. It follows that the gyrovibronic origin of band $C_0$ is at 42,267 cm.$^{-1}$. Some of this energy is due to rotation, and, allowance being made for this, we find for the vibronic origin of the C progression, which is the electronic origin of the band-system in dideuteroacetylene, the value 42,260 cm.$^{-1}$.

The relation of this figure for dideuteroacetylene to that derived above for acetylene is so reasonable as to leave no doubt that quantum numbers have been assigned, and the electronic origin for dideuteroacetylene has been located, correctly. Our closest guide is that of benzene. The difference of zero-point energy between benzene and hexadeuterobenzene in the electronic ground state is 4100 cm.$^{-1}$; and, in an excitation by 38,000 cm.$^{-1}$, this difference drops by 5%, with the result that the origin of the band-system of hexadeuterobenzene is displaced to a higher frequency than that of benzene by 200 cm.$^{-1}$ (Garforth, Ingold, and Poole, *J.*, 1948, 515). The difference of zero-point energy between acetylene and dideuteroacetylene in the electronic ground state is 1156 cm.$^{-1}$ (Table 9, p. 2716). Naively, we might expect that an excitation of 42,000 cm.$^{-1}$ would reduce the difference by 5½%, thus to displace the origin of the band-system of dideuterobenzene to higher frequency than that of acetylene by 64 cm.$^{-1}$. The displacement deduced above is in the expected sense and amounts to 62 cm.$^{-1}$. Discrepancies of hundreds of cm.$^{-1}$ would have arisen if any quantum numbers had been misassigned.

(j) *The Intensity of the Band-system.*—In acetylene at ordinary temperature about 88% of the molecules are in the vibrationless electronic ground state $\Sigma_g^+$. Nearly all of those excitations to the bent electronic state $A_u$ which start without vibrations, end to give the bands of progression C, the other progressions having a vibrationless starting state, D and c, being relatively quite weak. Hence the intensity of the C progression, calculated with due allowance for the proportion of molecules available to produce it, can be taken as an approximation to the intensity of the whole electronic transition.

As mentioned in Part III (p. 2717), we have measured, by the method described in Part II (p. 2707), the intensities of the bands of this progression from $C_1$ to $C_5$. The results, expressed as oscillator-strengths, which allow for the circumstance that not all the molecules present are in the relevant initial state, are given in Table 19. From the variation of oscillator-strength with quantum number, we have calculated, in the simplified way outlined in Part III (p. 2717), the overlap parameter $q$, which is the displacement of origin of the appropriate vibrational co-ordinates in the combining states. As there are three vibrations in the totally symmetric species of the bent state, $q$ is a somewhat involved function of its geometry: indeed, in order to deduce this function, it is necessary to know

the force system. But the determination of $q$ from band intensities allows us to use the sum rule, and thus to calculate, as described in Part III (p. 2717), from the intensity of each measured band, the intensity of the whole C progression. The results of these calculations are seen to be fairly consistent from the following:

*Oscillator-strengths (f) of* C *bands and of* C *progression.*

| Band | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ |
|---|---|---|---|---|---|
| $10^5 f$ measured for band | 0·0042 | 0·036 | 0·145 | 0·51 | 1·2 |
| $10^5 f$ calc. for progression | 7·9 | 9·5 | 8·2 | 8·4 | 6·4 |

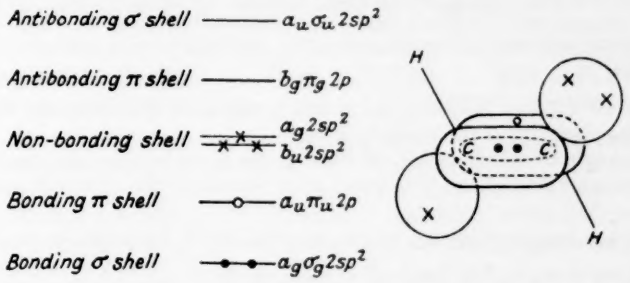
The oscillator-strength of the C progression is thus about $8 \times 10^{-5}$, this figure containing an allowance for the circumstance that, under the conditions of measurement, not all the molecules are in the starting state. The same figure, preferably in its rounded form $1 \times 10^{-4}$, should represent an approximation to the oscillator-strength of the whole electronic transition.

An ordinary allowed electric-dipole transition often has an oscillator-strength of 0·1—1. The result that our transition is $10^3$—$10^4$ times weaker is not due to its being forbidden in any way by the symmetry of the combining states. The transition is what we might call " Franck–Condon-forbidden." In other words, the change of shape is so drastic (as we shall particularise later) that the transitions are far from being " vertical " transitions in the Franck sense. Quantally, this diminishes their probability. Classically, the electron-jump is reduced to slow motion by the need to wait for the nuclei.

### (4) Physical nature of the excited state

(a) *Electronic Properties.*—Here we shall collect the conclusions which have already been reached, though some have not yet been put into words. The upper electronic state of the near-ultra-violet band-system of acetylene has the *trans*-bent stereochemical configuration, and the electronic wave-function has the symmetry of the model of the molecule, except that it changes sign across the molecular plane, to which the oscillatory transition moment is perpendicular.

Fig. 13. *Schematic representation of orbital occupancy in the upper electronic state of the near-ultra-violet band-system of acetylene. The carbon atoms are bound by three shared electrons and possess 1·5 unshared electrons each in* trans*-related groups, weak resonance being assumed between the non-bonding atomic orbitals sketched, to give the molecular non-bonding orbitals named.*




The electronic configuration adopted in the bent upper state by the six electrons of the original carbon triple bond is as shown schematically in Fig. 13. On the left an orbital energy diagram indicates the occupancy of the successive shells, while the sketch on the right is a reminder of the general geometrical relation of the occupied orbitals. As the antibonding shells are unoccupied, the configuration represents a 3-electron C–C bond, and we ought to expect its length and force-constant to correspond to a bond-multiplicity of 1·5. The two carbon atoms between them have three essentially unshared electrons, and, allowing for the expected weak resonance between the non-bonding atomic orbitals, we may say that each carbon atom has 1·5 unshared electrons. The two groups of unshared electrons are *trans*-related, and, in the light of dispersion theory, this has an important bearing on the directed polarisability of the carbon atoms of normal acetylene.

(b) *Geometrical Properties.*—The rotational constants $A$ for the electronic upper state of acetylene in several different states of vibration are given in Table 17. They may also be obtained by the nearly independent method of adding to the values of $\{A - \frac{1}{2}(B + C)\}$ given in Table 18 the relatively small and nearly constant values of $\frac{1}{2}(B + C)$ obtained from Table 17. The mean values of $A$ obtained in these ways are given in Table 19, and,

TABLE 19. *Mean rotational constants* A *(in cm.$^{-1}$) for the bent excited states of acetylene and dideuteroacetylene.*

| $v$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| $C_2H_2$ ..... | 12·50 | 13·81 | 15·14 | 16·34 | 17·70 | — | — |
| $C_2D_2$ ..... | — | — | 9·31 | 9·86 | 10·41 | 10·82 | 11·03 |

as shown in Fig. 14, they plot to a good straight line, from which smoothed values can be read. Slightly better values of the other rotational constants, $B$ and $C$, than those in Table 17, may be similarly deduced by plotting.

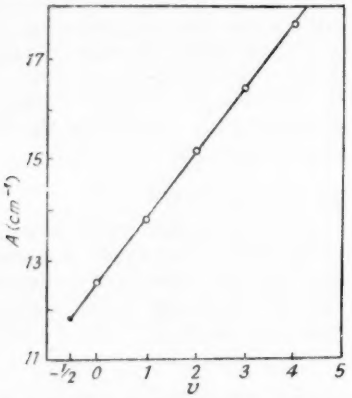



FIG. 14. *Variation of the rotational constant* A *of the* trans*-bent electronic upper state of acetylene with the quantum number* v *of its totally symmetrical bending vibration.*

The values adopted as a result of these procedures for $A^{(0)}$, $B^{(0)}$, and $C^{(0)}$, the rotational constants of the vibrational ground state of the electronically excited molecule are:

$$A^{(0)} = 12{\cdot}50, \qquad B^{(0)} = 1{\cdot}127, \qquad C^{(0)} = 1{\cdot}033 \text{ cm.}^{-1}$$

The corresponding moments of inertia are:

$$10^{40}I_a^{(0)} = 2{\cdot}24 \qquad 10^{40}I_b^{(0)} = 24{\cdot}83 \qquad 10^{40}I_c^{(0)} = 27{\cdot}09 \text{ g.-cm.}^2$$

We note that $10^{40}(I_a^{(0)} + I_b^{(0)}) = 27{\cdot}07$ g.-cm.$^2$, which agrees so nearly with $10^{40}I_c^{(0)}$ as to establish the planarity of the excited molecule.

If $\alpha$ is the angle by which each C–H bond in the *trans*-bent excited molecule is turned out of the produced line of the C–C bond, then the moments of inertia are given by the formulæ:

$$I_a = \tfrac{1}{2}(m_C + m_H)r_{CC}^2 \sin^2\theta + 2m_H r_{CH}^2 \sin^2(\alpha - \theta) - 2m_H r_{CC} r_{CH} \sin\theta \sin(\alpha - \theta)$$
$$I_c = \tfrac{1}{2}(m_C + m_H)r_{CC}^2 + 2m_H r_{CH}^2 + m_H r_{CC} r_{CH} \cos\alpha$$
$$I_b = I_c - I_a$$

Here $m_C$ and $m_H$ are the atomic masses, and $r_{CC}$ and $r_{CH}$ the bond lengths, while $\theta$, the angle between the C–C bond and the principal axis of inertia $a$, is given by

$$\tan 2\theta = \frac{m_H r_{CH}^2 \sin 2\alpha + m_H r_{CC} r_{CH} \sin\alpha}{\frac{1}{4}(m_C + m_H)r_{CC}^2 + m_H r_{CH}^2 \cos 2\alpha + m_H r_{CC} r_{CH} \cos\alpha}$$

Various bond lengths and bond angles were assumed and the corresponding moments of inertia were calculated, until agreement with the spectroscopically determined values were obtained. Some of these calculated values are in Table 20, line (6) of which represents our best approximation.

Actually, the three geometrical parameters, $r_{CC}$, $r_{CH}$, and $\alpha$, cannot uniquely be

determined from the moments of inertia of excited acetylene only, because, in this planar molecule, but two of the three moments are independent. We could, for example, change $r_{CH}$ slightly from 1·08 Å, and make compensating adjustments in $r_{CC}$ and $\alpha$. However, the choice $r_{CH} = 1{\cdot}08$ Å can be supported by reference to the spectrum of dideuteroacetylene. Here we have values of $\{A - \frac{1}{2}(B + C)\}$ for various vibrational quantum numbers $v$. The unimportant part of this, $\frac{1}{2}(B + C)$, which we know to be practically independent of $v$, can be computed sufficiently well from the calculated moments of inertia $I_b$ and $I_c$ of Table 20. This leaves the main term $A$, essentially spectroscopic in its mode of determination, as already recorded in Table 19. This quantity depends markedly on $v$; but a graphical extrapolation, which is not quite linear, probably because of the use of R-heads, instead of Q-heads, in the measurements of $\{A - \frac{1}{2}(B + C)\}$ in this spectrum, allows us to deduce $A^{(0)}$, and thence that $10^{40}I_a^{(0)} = 3{\cdot}50$ g.-cm.$^2$, in agreement with the calculated value in line (10) of Table 20.

TABLE 20. *Calculated moments of inertia (I in g.-cm.$^2$) of the* trans*-bent molecule: comparison with spectroscopic values.*

| | $r_{CC}$ | $r_{CH}$ | $\alpha$ | $\theta$ | $10^{40}I_a$ | $10^{40}I_b$ | $10^{40}I_c$ |
|---|---|---|---|---|---|---|---|
| | | | | *Acetylene* | | | |
| (1) | 1·40 | 1·06 | 63° | 9° 42′ | 2·35 | 24·84 | 27·19 |
| (2) | 1·40 | 1·08 | 63° | 9° 57′ | 2·43 | 24·95 | 27·38 |
| (3) | 1·39 | 1·08 | 62° | 10° 1′ | 2·37 | 24·76 | 27·14 |
| (4) | 1·38 | 1·08 | 62° | 10° 7′ | 2·36 | 24·46 | 26·82 |
| (5) | 1·38 | 1·08 | 60° | 10° 1′ | 2·25 | 24·72 | 26·97 |
| (6) | 1·383 | 1·08 | 59° 50′ | 9° 58′ | 2·24 | 24·84 | 27·08 |
| | | | | Spectrosc. | 2·24 | 24·83 | 27·09 |
| | | | | *Dideuteroacetylene* | | | |
| (7) | 1·40 | 1·06 | 63° | 14° 50′ | 3·99 | 34·16 | 38·16 |
| (8) | 1·39 | 1·08 | 62° | 16° 55′ | 3·75 | 31·26 | 35·00 |
| (9) | 1·38 | 1·08 | 60° | 16° 45′ | 3·53 | 31·42 | 34·96 |
| (10) | 1·383 | 1·08 | 59° 50′ | 16° 40′ | 3·51 | 31·49 | 35·00 |
| | | | | Spectrosc. | 3·50 | — | — |

The significance of this check may be explained as follows. Suppose that we have been taking $r_{CH}$ too small in acetylene. Then all three moments of inertia must be too small. But we can make them right by taking, judiciously, $r_{CC}$ too large and $\alpha$ too wide. However, when we now take $r_{CH}$ equally too small in dideuteroacetylene, we are bringing in from the periphery of the molecule towards its centre of gravity twice as much mass as before, and therefore the same adjustments in $r_{CC}$ and $\alpha$ will not compensate.

We conclude that the geometrical form of the *trans*-bent molecule is given approximately by the following figures:

$$r_{CC} = 1{\cdot}383 \text{ Å} \qquad r_{CH} = 1{\cdot}08 \text{ Å} \qquad \angle CCH = 120{\cdot}2°$$

The value for the valency angle implies that the change of σ-bond hybridisation from linear to plane-trigonal during the electronic excitation is complete. It is consistent with our conclusions concerning the configuration to which the π electron system is excited, a configuration involving a 3-electron C–C bond, that the length of the C–C bond is almost as in benzene, the geometrical parameters of which are usually given as $r_{CC} = 1{\cdot}39$ Å, $r_{CH} = 1{\cdot}08$ Å, $\angle CCH = 120°$.

In Fig. 15 the nuclear distributions of the normal and the excited molecule of acetylene are drawn to scale with coincident axes of inertia. From the drawing one can see in what directions and how far the atoms have to move when excitation takes place from one vibrationless form to the other as at the origin of the band system. It is easy to appreciate from this diagram why the $\Pi_g$ or $A_g(\alpha)$ vibration is so very much more intensity-giving than either of the other vibrations $\Sigma_g^+(C)$ or $A_g(C)$, and $\Sigma_g^+(H)$ or $A_g(H)$, which on grounds of symmetry alone, are equally competent to form bands.

(c) *Elastic Properties.*—From the Tables in Part V (following paper), it is possible directly to read the fundamental frequencies of the vibrations $A_g(\alpha)$ and $A_g(C)$ of the excited acetylene molecule, that is, the size of the first quantum of each of these vibrations in the absence of all other vibrations. The same two fundamental frequencies can be determined with fairly close approximation for excited dideuteroacetylene from higher

harmonics of $A_g(\alpha)$, and from combination frequencies of $A_g(\alpha)$ with $A_g$(C), by back-extrapolation over the first two quanta of $A_g(\alpha)$. A similar procedure of extrapolations allows us to find the fundamental frequency $A_g$(H) of excited dideuteroacetylene. These frequencies are in Table 21.

TABLE 21. *Totally symmetrical fundamental frequencies (cm.$^{-1}$) of the* trans*-bent excited states of acetylene and dideuteroacetylene.*

| | $A_g(\alpha)$ | $A_g$(C) | $A_g$(H) |
|---|---|---|---|
| $A_u$ state of $C_2H_2$ ..... | 1049 | 1380 | (3020, 2980) |
| " " $C_2D_2$ ..... | 844 | 1310 | 2215 |

We have no similarly direct method of deducing the fundamental frequency $A_g$(H) of excited acetylene, but we have two rough and indirect methods, which agree tolerably well, and give a mean result of 3000 cm.$^{-1}$. The first method is based on the hypothesis that the perturbations, observed in C bands above $C_3$, are due to Fermi resonance with transitions involving the development in absorption of one quantum of the vibration $A_g$(H). By noting the magnitudes and directions (up in $C_4$ and down in $C_5$, for example) in which line positions are shifted from the expected positions, and allowing an effect of anharmonicity on $A_g(\alpha)$–$A_g$(H) combination frequencies in acetylene on the basis of

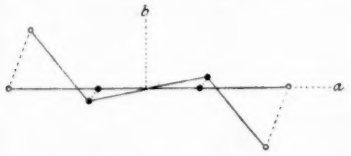



FIG. 15. *The linear normal and* trans*-bent excited molecules of acetylene on the same scale and with coincident axes of inertia.*

what we know of such an effect in dideuteroacetylene, we can approximately locate the unperturbed positions of the perturbing bands, and thereby deduce that the fundamental frequency of the vibration $A_g$(H) of acetylene is about 3020 cm.$^{-1}$. The other method is to use the product rule of Teller and Redlich in its application to the excited acetylene molecule. This theorem requires that the ratio of the $A_g$ frequency-products of the light and the heavy molecule shall be twice the square-root of the ratio of their moments of inertia around axis *c*. Taking the moments of inertia from Table 20, we can easily deduce that the acetylene frequency $A_g$(H) required to give the right product ratio is 2980 cm.$^{-1}$.

From the carbon stretching frequencies, we can deduce that the carbon-bond force-constant of excited acetylene is $7{\cdot}2 \times 10^5$ dynes/cm. Since the usually given force constant for a single carbon bond is $4{\cdot}5 \times 10^5$, and for a double bond $9{\cdot}8 \times 10^5$ dynes/cm., the value at which we have arrived, namely, the mean of these, seems a fortunate one to be able to offer for a three-electron bond. The value for normal benzene is $7{\cdot}6 \times 10^5$ dynes/cm. From the hydrogen-stretching frequencies, the force constant of the C–H bond of the excited acetylene molecule is computed to be $5{\cdot}0 \times 10^5$ dynes/cm. This should be compared with the CH constants of those normal molecules, such as benzene and ethylene, whose structures are based on plane-trigonal hybridisation : for both the CH force-constant is given as $5{\cdot}1 \times 10^5$ dynes/cm. The calculated bending force-constant of excited acetylene is somewhat sensitive to the precise method of calculation, but in view of the incompleteness of our knowledge of the potential-energy function, the simplest possible method (assuming independent hydrogen motions with non-stretching bonds) is not demonstrably worse than any other. It gives for the bending moment constant of excited acetylene $8 \times 10^{-12}$ dyne-cm./radian. The value for planar hydrogen-bending motion in benzene, the most nearly comparable normal molecule with respect to *both* bonds forming the variable angle, is given also as $8 \times 10^{-12}$ dyne-cm./radian.

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## 553. *Excited States of Acetylene. Part V.* Measured and Calculated Frequencies in the Near-ultra-violet Absorption Spectra of Acetylene and Dideuteroacetylene: Vibrational and Rotational Energies of the* trans-*Bent Excited State.*

By C. K. Ingold and G. W. King.

Band and line frequencies are recorded which lead to vibrational frequencies of the excited states, and to their rotational constants. The results of some calculations are given on which rotational line assignments are based.

### (1) Vibrational analysis

(a) *Normal Electronic State.*—The present spectra provide an opportunity for learning one new thing about the already very closely studied vibrations of the ground state of acetylene, namely, the variation of magnitude of successive quanta of the bending vibration $\pi_g$. As appears from Table 22, this vibration shows the opposite of the usual trend, its energy in acetylene *increasing* by about 1% per quantum over the first three quanta, and in dideuteroacetylene by slightly less than this. The trends suggest that the wall of resistance to hydrogen bending hardens somewhat sharply as the amplitude is increased.

Table 22. *Energies (cm.$^{-1}$) of the $\pi_g$ vibration of normal acetylene and dideuteroacetylene.*

[$v$ is the total and $K$ the azimuthal quantum number of this vibration, while $v'$ is the quantum number with which vibration $A_g$ ($\alpha$) is also excited in the measured bands.]

| | Quantum $Q_1$ between quantum numbers ($v^K$) : $1^1 - 0^0$ | | Quantum $Q_2$ between quantum numbers ($v^K$) : $2^2 - 1^1$ (two estimates) | | | |
|---|---|---|---|---|---|---|
| | Band D — band B | | Band G — band H | | Band C — band E — $Q_1$ | |
| $v'$ | $C_2H_2$ | $C_2D_2$ | $C_2H_2$ | $C_2D_2$ | $C_2H_2$ | $C_2D_2$ |
| 1 | 612·1 | — | 617·6 | — | 618·9 | — |
| 2 | 612·5 | 510·5 | 617·3 | — | 619·5 | 513·2 |
| 3 | 611·2 | 510·6 | 620·9 | — | 621·2 | 512·9 |
| 4 | 610·7 | 510·3 | 621·1 | 511·5 | 619·2 | 513·0 |
| 5 | — | 510·8 | — | 513·5 | — | 513·5 |

| | Quantum $Q_3$ between quantum numbers ($v^K$) : $3^1 - 2^2$ (two estimates) | | | |
|---|---|---|---|---|
| | Band A — band J — $Q_2$ | | Band B — band F — $Q_2$ | |
| $v'$ | $C_2H_2$ | $C_2D_2$ | $C_2H_2$ | $C_2D_2$ |
| 2 | 624·7 | 518·0 | 624·5 | 518·3 |
| 3 | 623·0 | 517·4 | 622·6 | 517·7 |
| 4 | — | 518·4 | 624·1 | 518·6 |
| 5 | — | 517·1 | — | 517·4 |

(b) *The Excited Electronic State.*—The vibration $A_g(\alpha)$ can be measured over the first five quanta in acetylene, and over four quanta, starting with the third, in dideuteroacetylene. The most direct source of data consists of the intervals in Table 23 between successive C

Table 23. *Energies (cm.$^{-1}$) of $A_g(\alpha)$ vibration of excited acetylene and dideuteroacetylene.*

| | $C_1 - C_0$ | $C_2 - C_1$ | $C_3 - C_2$ | $C_4 - C_3$ | $C_5 - C_4$ | $C_6 - C_5$ |
|---|---|---|---|---|---|---|
| $C_2H_2$ ..... | 1048·7 | 1032·1 | 1011·8 | 986·0 | 972·5 | — |
| $C_2D_2$ ..... | — | — | 823·8 | 814·4 | 802·6 | 781·4 |

bands, though it must be remembered that the acetylene bands $C_4$ and $C_5$ are appreciably perturbed. For both molecules the energies of successively added quanta fall by about 1·7% for each extra quantum.

* Part IV, preceding paper.

For both acetylene and dideuteroacetylene, the energy of the first quantum of vibration $A_g$(C) may be deduced from the frequencies of combinations with various quanta of vibration $A_g(\alpha)$, as is shown in Table 24. For dideuteroacetylene only, the energy of the first quantum of vibration $A_g$(H) can be similarly obtained, as shown in Table 25.

TABLE 24. *Energy (cm.$^{-1}$) of the first quantum of vibration* $A_g$(C).

[$v'$ is the quantum number with which vibration $A_g(\alpha)$ is simultaneously excited.]

| $v'$ | a − A | b − B | c − C | e − E | f − F | j − J | h − H |
|---|---|---|---|---|---|---|---|
| | | | *Acetylene* | | | | |
| 0 | 1379·0 | 1385·3 | — | — | — | — | — |
| 1 | 1382·6 | 1384·2 | 1384·1 | 1384·8 | — | — | 1381·7 |
| 2 | 1383·0 | 1386·1 | 1385·8 | 1385·5 | 1384·6 | 1386·4 | 1384·1 |
| 3 | 1385·4 | 1384·3 | 1384·6 | 1385·4 | 1384·5 | 1381·4 | 1382·7 |
| 4 | 1386·3 | 1384·4 | — | 1387·0 | 1385·4 | 1382·2 | 1387·9 |
| 5 | — | — | — | — | 1385·7 | — | — |
| | | | *Dideuteroacetylene* | | | | |
| 2 | 1299·8 | 1298·5 | 1299·3 | 1299·1 | 1298·4 | 1300·1 | — |
| 3 | 1295·4 | 1293·0 | 1294·2 | 1293·3 | — | 1294·4 | — |
| 4 | 1291·1 | 1289·1 | 1291·0 | 1289·0 | — | 1290·4 | — |
| 5 | 1288·5 | 1286·5 | — | 1288·6 | 1286·1 | — | — |

(Additional values for acetylene from "hot" bands: $h_1 - K_1 = 1381{\cdot}6$ cm.$^{-1}$; $l_1 - L_1 = 1385{\cdot}0$ cm.$^{-1}$.)

TABLE 25. *Energy (cm.$^{-1}$) of first quantum of vibration* $A_g$(H) *of dideuteroacetylene.*

($v'$ is the quantum number with which vibration $A_g(\alpha)$ is simultaneously excited.)

| $v'$ | p − A | q − B | r − C | t − E | u − F | w − H | y − J |
|---|---|---|---|---|---|---|---|
| 2 | 2198·1 | 2198·6 | — | 2197·7 | 2200·2 | — | 2198·1 |
| 3 | 2191·2 | 2191·8 | 2191·6 | 2190·6 | — | 2191·5 | 2190·4 |
| 4 | 2183·1 | 2180·0 | — | — | — | — | — |

## (2) ROTATIONAL ANALYSIS

For the normal acetylene molecule, we have taken the standard value $B'' = 1{\cdot}1769$ cm.$^{-1}$ as the rotational constant applying to all the vibrational states of concern to us. As to the bent excited molecule, the rotational constant $A$, depending as it does on an average departure from linearity, is quite a sensitive function of the number of quanta with which the vibration $A_g(\alpha)$ is excited; while the constants $B$ and $C$, depending as they do on an average molcular length, have a small but appreciable dependence on the vibration $A_g(\alpha)$. Thus for each value $v'$ of the quantum member of this vibration, that is, for each repetition of the gyrovibronic pattern of bands, D, C, G, B, A, H, E, F, J, etc., we have to

TABLE 26. *Calculated and observed line positions of band* $C_1$.

Spectral positions are in cm.$^{-1}$, but in the columns only the last three significant figures are noted. Lower state, $B'' = 1{\cdot}1769$ cm.$^{-1}$. Upper state, $A = 13{\cdot}80$ cm.$^{-1}$, $B = 1{\cdot}126$ cm.$^{-1}$, $C = 1{\cdot}030$ cm.$^{-1}$. Vibronic origin, $\nu_{00} = 43{,}245{\cdot}0$ cm.$^{-1}$. Gyrovibronic origin, $\nu_0 = 43{,}257{\cdot}7$ cm.$^{-1}$.

| | R Branch | | Q Branch | | P Branch | |
|---|---|---|---|---|---|---|
| $J''$ | Calc. | Obsd. | Calc. | Obsd. | Calc. | Obsd. |
| 0 | 59·9 | — | — | — | — | — |
| 1 | 62·2 | 62·2 | 57·5 | 56·5 | — | — |
| 2 | 63·9 | — | 56·9 | | 52·9 | — |
| 3 | 65·8 | 66·2 | 56·2 | | 50·4 | (50·9) |
| 4 | 67·2 | — | 55·3 | — | 47·4 | — |
| 5 | 68·9 | 69·0 | 54·0 | 54·1 | 44·7 | 44·4 |
| 6 | 69·8 | — | 52·5 | — | 41·3 | (41·4) |
| 7 | 71·1 | 73·9 head | 50·8 | 50·9 | 38·3 | 38·3 |
| 8 | 72·2 | | 48·2 | — | 34·5 | (35·0) |
| 9 | 73·1 | | 46·5 | 46·7 | 31·1 | 31·4 |
| 10 | 73·7 | | 44·1 | (44·4) | 27·5 | (27·6) |
| 11 | 74·0 | | 41·1 | 41·4 | 23·6 | 23·6 |
| 12 | — | — | 38·2 | (38·3) | 19·6 | (19·4) |
| 13 | — | — | — | — | 15·2 | 15·5 |

determine a new set of constants $A$, $B$, $C$, such that, when they are introduced into the exact energy expression for the asymmetric rotor, they will yield energy levels so spaced relatively to the rotational levels of the linear ground molecule, as to give line positions agreeing with the observed fine structure. Examples are given in Tables 26, 27, and 28 of such calculations for three bands, $C_1$, $A_1$, and $B_1$, all of the one-quantum gyrovibronic pattern. The same rotational constants have been used in calculations, not illustrated, on the bands $E_1$, $H_1$, $D_1$, and $G_1$, of the same pattern, $v' = 1$. Similarly determined rotational constants, applying to the other gyrovibronic patterns, having quantum numbers $v'$ from 0 to 3, are listed in Part IV, Table 17, p. 2735.

TABLE 27. *Calculated and observed line positions of band* $A_1$.

See notes at head of Table 26. Rotational constants as there stated. Vibronic origin $\nu_{00} = 42{,}633{\cdot}0$ cm.$^{-1}$. Gyrovibronic origin $\nu_0 = 42{,}633{\cdot}0$ cm.$^{-1}$.

| | R Branch | | Q Branch | | P Branch | |
|---|---|---|---|---|---|---|
| $J''$ | Calc. | Obsd. | Calc. | Obsd. | Calc. | Obsd. |
| 0 | — | — | — | — | — | — |
| 1 | — | — | 32·8 | | 30·1 | — |
| 2 | — | — | 32·4 | | 28·1 | 28·3 |
| 3 | — | — | 31·8 | 31·9 | 25·3 | — |
| 4 | — | — | 31·0 | | 22·4 | 23·8 |
| 5 | — | — | 30·0 | 30·1 | 19·3 | (19·8) |
| 6 | 43·7 | | 28·7 | — | 15·7 | 16·0 |
| 7 | 44·4 | | 27·2 | 28·3 | 12·3 | (12·1) |
| 8 | 44·7 | 44·5 | 25·5 | — | 08·4 | 08·3 |
| 9 | 44·9 | (head) | 23·6 | 23·8 | 04·4 | (04·6) |
| 10 | 44·7 | | 21·3 | — | 00·0 | 00·4 |
| 11 | 44·0 | | 18·8 | 19·8 | 95·9 | — |
| 12 | — | — | 16·1 | (16·0) | 90·5 | 91·2 |
| 13 | — | — | — | — | 85·5 | (87·3) |

TABLE 28. *Calculated and observed line positions of band* $B_1$.

See notes at head of Table 26. Rotational constants as there stated. Vibronic origin, $\nu_{00} = 42{,}633{\cdot}0$ cm.$^{-1}$. Gyrovibronic origin, $\nu_0 = 42{,}683{\cdot}9$ cm.$^{-1}$.

| | R Branch | | Q Branch | | P Branch | |
|---|---|---|---|---|---|---|
| $J''$ | Calc. | Obsd. | Calc. | Obsd. | Calc. | Obsd. |
| 0 | — | — | — | — | — | — |
| 1 | 88·0 | — | — | — | — | — |
| 2 | 89·8 | 90·8 | 83·3 | | | |
| 3 | 91·3 | | 82·7 | 82·7 | 76·2 | (77·6) |
| 4 | 92·8 | — | 81·9 | | 73·3 | 73·5 |
| 5 | 94·0 | — | 81·1 | 80·6 | 70·1 | — |
| 6 | 95·1 | — | 79·9 | | 67·0 | 68·3 |
| 7 | 95·9 | — | 78·6 | 77·6 | 63·2 | 63·0 |
| 8 | 96·8 | — | 76·8 | | 59·8 | 60·3 |
| 9 | 97·5 | 97·1 | 75·0 | — | 55·6 | 56·8 |
| 10 | 98·1 | — | 73·0 | — | 52·9 | 52·9 |
| 11 | 98·5 | — | 72·2 | — | 47·1 | 48·4 |
| 12 | — | — | 70·2 | — | 44·0 | Overlap |
| 13 | — | — | — | — | 37·8 | with $A_1$ |

### (3) OBSERVED FREQUENCIES AND ASSIGNMENTS

The following four Tables, referring to the absorption spectra of acetylene and of dideuteroacetylene at 20° and 200°, contain the measured peak frequencies and our assignments of them. The indications of intensity, s = strong, w = weak, d = diffuse, etc., are to be understood as applying relatively to the immediate spectral surroundings of any maximum so marked. The grouping of the maxima in bands is indicated by the labelled R-head, with which each band starts, when the observations are arranged, as here, in order of decreasing frequency. The labels of the assigned bands are placed opposite the frequencies of their R-heads. Almost all the clearly defined bands in these spectra have been assigned, excepting a few near the beginnings of Tables 29 and 31, which probably belong to gyrovibronic patterns headed by C bands lying beyond the high-frequency limits of the observed spectra.

TABLE 29. *Frequencies (cm.$^{-1}$) of absorption maxima of acetylene at 20°.*

| Frequency | Assignment Band | Lines | Frequency | Assignment Band | Lines | Frequency | Assignment Band | Lines |
|---|---|---|---|---|---|---|---|---|
| **47,315·3** wd | $D_5$ | R-head | 50·6 s | — | R-head | 44·6 s | | |
| **47,282·9** w | | | 46·8 w | | | 39·3 | | |
| 79·4 w | | | 43·2 | | | 35·0 ss | $A_5$ | R-head |
| 75·2 ss | $C_5$ | R-head | 38·9 | | | 29·3 | | |
| 67·3 | | | 32·2 | | | 23·8 ss | — | Q-head |
| 59·1 s | — | Q-head | 29·4 sd | | | 21·2 | | |
| 56·6 | | | 27·0 | | | 17·2 | | |
| 52·8 | | | 21·8 s | | | 13·9 | | |
| 50·1 | | | 16·6 s | | | 10·4 | | |
| 47·6 s | | | 13·2 | | | 07·4 | | |
| 42·5 | | | 10·3 | | | 04·6 | | |
| 40·3 | | | 04·2 | | | 02·2 wd | | |
| 35·9 | | | **46,888·0** | | | **46,599·7** | | |
| 32·8 | | | 84·6 | | | 97·8 | | |
| 27·9 | | | 82·0 | | | 93·6 s | | |
| 23·8 ss | — | R-head | 77·4 ss | — | | 91·1 s | $h_4$ | R-head |
| 18·7 | | | 74·2 | | | 86·4 s | | |
| 14·9 | | | 69·0 w | | | 82·3 d | | |
| 09·4 | | | 60·2 s | | | 77·4 | | |
| 04·3 s | | | 54·6 s | | | 73·0 | | |
| **47,199·1** | | | 50·9 s | $f_5$ | R-head | 71·5 | | |
| 96·2 | | | 46·7 | | | 68·9 w | | |
| 92·5 | | | 43·1 | | | 65·5 | | |
| 89·9 | | | 40·7 | | | 63·3 | | |
| 86·4 s | | | 34·8 ss | | | 60·8 | | |
| 83·4 | | | 30·5 s | | | 57·4 | | |
| 79·9 | | | 26·9 w | | | 53·0 wd | | |
| 75·6 | | | 18·1 | | | 49·5 | | |
| 72·2 | | | 12·5 ss | | | 40·1 s | | |
| 67·3 | | | 09·9 | | | 32·9 s | | |
| 63·9 s | — | R-head | 07·3 ss | | | 29·8 w | | |
| 60·8 | | | 04·1 ss | | | 27·8 w | | |
| 58·1 | | | **46,796·7** | | | 25·8 | | |
| 54·5 | | | 89·7 ss | $G_5$ | | 23·9 | | |
| 45·6 | | | 87·6 s | | | 19·9 s | | |
| 42·8 | | | 85·5 | | | 18·0 s | | |
| 40·2 | | | 80·6 | | | 11·7 | | |
| 35·3 | | | 77·7 | | | 07·8 w | | |
| 30·0 | | | 74·7 s | | | 05·1 | | |
| 23·6 ss | $b_4$ | R-head | 68·1 s | | | 03·8 | | |
| 20·2 | | | 65·7 w | | | 01·0 w | | |
| 17·2 | | | 64·3 w | | | **46,498·1** | | |
| 11·8 | — | Q-head | 60·7 s | | | 96·0 | | |
| 07·8 | | | 53·7 ss | — | R-head | 91·7 w | | |
| 04·8 | | | 49·9 | | | 87·8 w | | |
| 00·0 | | | 43·8 | — | Q-head | 79·1 s | — | R-head |
| **47,095·8** | | | 42·3 | | | 76·0 | | |
| 92·5 | | | 40·0 | | | 73·7 w | | |
| 88·4 s | | | 37·1 | | | 71·5 w | | |
| 80·7 | | | 35·2 | | | 68·7 | | |
| 74·2 | | | 33·2 | | | 67·5 | | |
| 69·9 | | | 29·0 | | | 63·6 w | | |
| 64·3 | | | 24·2 | | | 60·4 ss | $e_4$ | R-head |
| 56·6 s | $a_4$ | R-head | 17·3 s | | | 57·4 | | |
| 45·5 | — | Q-head | 13·9 | | | 54·6 w | | |
| 43·3 s | | | 09·8 s | | | 46·6 s | — | Q-head |
| 40·7 | | | 02·4 ss | $c_3 + B_5$ | R-head | 44·6 s | | |
| 36·6 s | | | **46,695·7** s | | | 42·9 s | | |
| 31·8 | | | 89·9 | | | 40·7 s | | |
| 30·0 | | | 85·6 s | — | Q-head | 38·8 w | | |
| 25·7 | | | 83·0 | | | 35·9 w | | |
| 22·5 | | | 79·1 | | | 34·0 s | | |
| 19·0 | | | 77·2 w | | | 30·1 s | | |
| 13·1 | | | 74·2 | | | 27·9 sd | | |
| 03·2 | | | 68·8 s | | | 24·2 w | | |
| **46,993·1** | | | 65·4 | | | 21·8 w | | |
| 72·9 | | | 61·8 s | | | 19·0 s | | |
| 69·0 | | | 57·7 | | | 14·4 | | |
| 65·7 | | | 53·8 s | | | 11·7 | | |
| 60·5 | | | 49·4 | | | 07·9 w | | |

TABLE 29.—*Continued.*

| Frequency | Assignment Band | Assignment Lines |
|---|---|---|
| 05·9 w | | |
| 02·1 s | | |
| 46,397·0 s | | |
| 92·4 s | | |
| 89·0 w | | |
| 83·9 w | | |
| 81·6 s | | |
| 78·8 | | |
| 75·9 | | |
| 73·5 | | |
| 70·4 | | |
| 63·9 | | |
| 57·8 | | |
| 53·2 | | |
| 49·9 s | $D_4$ | R-head |
| 47·8 | | |
| 44·7 | | |
| 41·2 | | |
| 36·5 | | |
| 24·9 | | |
| 20·2 | | |
| 17·3 | | |
| 14·3 | | |
| 03·3 ss | $C_4$ | R-head |
| 46,299·8 s | | |
| 96·1 | | |
| 92·1 | | |
| 86·5 s | — | Q1—3 |
| 84·1 s | — | Q5 |
| 80·7 s | — | Q7 |
| 78·1 | | |
| 75·7 sd | — | Q9, P5 |
| 70·6 | — | Q11 |
| 67·8 | — | P7 |
| 64·1 s | — | Q13 |
| 61·0 | — | P9 |
| 56·5 | — | Q15 |
| 53·6 | | |
| 51·9 w | | |
| 50·1 w | | |
| 47·4 | — | Q17 |
| 45·1 | | |
| 42·5 w | | |
| 40·9 w | | |
| 37·0 ss | | |
| 32·0 | | |
| 26·6 s | | |
| 23·4 w | | |
| 21·1 w | | |
| 18·2 | | |
| 16·3 | | |
| 14·5 | | |
| 07·1 s | $H_5$ | R-head |
| 06·3 s | | |
| 00·7 | | |
| 46,194·2 | | |
| 92·0 | | |
| 86·5 d | | |
| 72·6 s | | |
| 70·7 s | | |
| 68·2 w | | |
| 57·3 w | | |
| 53·6 w | | |
| 49·6 w | | |
| 43·3 | | |
| 37·5 | | |
| 31·7 ss | $b_3$ | R-head |
| 25·2 | | |
| 19·0 s | — | Q-head |
| 13·0 d | | |

| Frequency | Assignment Band | Assignment Lines |
|---|---|---|
| 11·3 | | |
| 07·1 | | |
| 03·3 | | |
| 00·3 | | |
| 46,096·3 s | | |
| 92·2 | | |
| 89·4 | | |
| 87·6 | | |
| 82·7 d | | |
| 78·0 | | |
| 70·8 ss | $a_3 + E_5$ | R-head |
| 67·7 | | |
| 62·9 | | |
| 59·3 s | — | Q-head |
| 57·2 | | |
| 50·5 s | | |
| 45·7 s | | |
| 43·2 s | | |
| 39·8 s | | |
| 36·5 w | | |
| 33·2 w | | |
| 26·4 d | | |
| 21·5 | | |
| 16·7 s | | |
| 06·2 s | | |
| 45,999·6 | | |
| 94·3 | | |
| 91·2 | | |
| 85·4 | | |
| 81·0 | | |
| 73·7 | | |
| 66·1 | | |
| 63·9 | | |
| 54·0 | | |
| 51·1 | | |
| 32·2 s | | |
| 29·0 s | | |
| 23·8 | | |
| 19·1 | | |
| 13·5 s | | |
| 08·4 | | |
| 03·2 | | |
| 45,880·2 ss | $f_4$ | R-head |
| 74·3 | | |
| 67·8 s | — | Q-head |
| 65·1 | | |
| 63·1 | | |
| 60·8 | | |
| 58·3 | | |
| 55·7 | | |
| 52·6 | | |
| 47·9 | | |
| 44·4 | | |
| 41·3 | | |
| 35·7 | | |
| 31·6 w | | |
| 28·9 | | |
| 24·3 s | $G_4$ | |
| 21·8 s | | |
| 13·1 s | | |
| 09·5 | | |
| 06·7 | | |
| 02·1 sd | | |
| 45,798·5 sd | | |
| 96·1 | | |
| 92·5 s | $j_4$ | R-head |
| 88·1 | | |
| 85·7 | | |
| 84·1 | | |
| 82·0 | | |

| Frequency | Assignment Band | Assignment Lines |
|---|---|---|
| 79·2 | | |
| 77·4 | | |
| 75·0 | | |
| 72·7 | | |
| 68·4 | | |
| 64·3 | | |
| 59·4 | | |
| 39·2 ss | $B_4$ | R-head |
| 31·1 | | |
| 27·9 | | |
| 25·6 s | — | Q-head |
| 23·2 | | |
| 19·7 | | |
| 15·4 | | |
| 10·4 | | |
| 04·3 | | |
| 45,698·5 | | |
| 91·1 ss | $c_3$ | R-head |
| 85·6 | | |
| 81·4 | | |
| 75·7 | | |
| 70·3 ss | $A_4$ | R-head |
| 65·2 | | |
| 58·1 s | — | Q-head |
| 56·8 sd | | |
| 53·6 | | |
| 49·5 | | |
| 45·7 w | | |
| 41·7 sd | | |
| 34·4 s | | |
| 30·4 w | | |
| 26·4 s | | |
| 21·9 w | | |
| 17·2 s | | |
| 13·6 w | | |
| 06·6 s | | |
| 02·9 w | | |
| 45,596·2 d | | |
| 94·1 | | |
| 89·1 s | $h_3$ | R-head |
| 84·2 | | |
| 81·5 | | |
| 77·4 | | |
| 75·5 s | | |
| 70·6 | | |
| 68·1 | | |
| 64·0 | | |
| 60·8 | | |
| 57·9 w | | |
| 55·5 w | | |
| 52·8 | | |
| 49·2 s | | |
| 44·9 | | |
| 40·4 w | | |
| 36·4 sd | | |
| 32·7 | | |
| 30·8 | | |
| 28·4 | | |
| 25·2 | | |
| 23·0 wd | | |
| 21·2 | | |
| 19·6 | | |
| 13·8 s | | |
| 01·3 | | |
| 45,470·8 ss | $e_3$ | R-head |
| 65·2 s | $F_5$ | |
| 59·9 | | |
| 55·2 s | | |
| 53·2 s | | |
| 50·2 | | |

TABLE 29.—*Continued.*

| Frequency | Assignment Band | Lines |
|---|---|---|
| 48·5 | | |
| 43·5 s | | |
| 40·1 | | |
| 38·2 | | |
| 34·4 | | |
| 33·4 wd | | |
| 30·6 s | | |
| 25·7 | | |
| 22·2 s | | |
| 16·4 | | |
| 12·9 s | | |
| 08·0 w | | |
| 06·2 w | | |
| 03·3 | | |
| 45,399·1 d | | |
| 92·7 s | | |
| 88·8 | | |
| 81·3 s | | |
| 76·9 | | |
| 72·8 | | |
| 68·3 | | |
| 58·6 ss | $D_3$ | R-head |
| 54·9 | | |
| 50·2 s | | |
| 45·9 | | |
| 41·3 | | |
| 37·9 | | |
| 34·0 | | |
| 28·9 | | |
| 26·3 | | |
| 23·1 | | |
| 17·8 ss | $C_3$ | R15 |
| 13·7 | — | R5, 7 |
| 10·1 | — | R3 |
| 06·5 | — | R1 |
| 00·5 s | — | Q1, 3 |
| 45,298·3 | — | Q5 |
| 94·7 | — | Q7 |
| 90·6 | — | Q9 |
| 88·6 w | — | P5 |
| 85·0 | — | Q11 |
| 82·3 w | — | P7 |
| 78·5 | — | Q13 |
| 75·2 w | — | P9 |
| 71·2 | — | Q15 |
| 67·5 w | — | P11 |
| 62·1 | — | Q17 |
| 60·1 | — | P13 |
| 52·2 | — | Q19 |
| 45·9 w | | |
| 41·4 s | — | Q21 |
| 35·1 w | | |
| 29·9 s | — | Q23 |
| 23·5 w | | |
| 18·3 | | |
| 15·1 | | |
| 12·8 w | | |
| 10·0 w | | |
| 03·2 ss | $H_4$ | R-head |
| 45,196·4 | | |
| 94·2 w | | |
| 88·3 sd | — | Q-head |
| 87·3 s | | |
| 85·0 s | | |
| 81·3 | | |
| 79·3 | | |
| 76·8 | | |
| 74·7 s | | |
| 71·2 wd | | |
| 64·3 wd | | |
| 59·9 | | |
| 17·3 ss | $b_2$ | R-head |
| 13·9 | | |
| 03·1 s | — | Q-head |
| 00·1 | | |
| 45,097·7 | | |
| 93·4 s | | |
| 88·5 s | | |
| 81·6 | | |
| 73·4 ss | $E_4$ | R-head |
| 68·9 s | | |
| 62·3 s | | |
| 57·2 s | $a_2$ | R-head |
| 52·6 | | |
| 50·7 | | |
| 47·6 | | |
| 42·0 s | | |
| 36·7 | | |
| 34·5 | | |
| 31·5 | | |
| 28·2 | | |
| 24·1 s | | |
| 19·5 | | |
| 15·6 | | |
| 09·2 | | |
| 05·2 | | |
| 44,996·3 d | | |
| 89·6 | | |
| 84·0 | | |
| 78·4 w | | |
| 71·9 s | | |
| 66·1 w | | |
| 59·1 | | |
| 44,888·2 ss | $f_3$ | R-head |
| 73·7 sd | | |
| 71·1 | | |
| 67·5 | | |
| 64·3 s | | |
| 60·6 d | | |
| 56·6 | | |
| 52·4 | | |
| 48·4 | | |
| 27·3 ss | $G_3$ | |
| 22·8 ss | $j_3$ | R-head |
| 14·9 d | | |
| 11·7 | | |
| 07·2 s | | |
| 02·7 | | |
| 44,799·7 | | |
| 96·8 w | | |
| 89·4 ss | | |
| 82·7 s | | |
| 47·4 ss | $B_3$ | ~R8 |
| 43·7 | — | R3, 4 |
| 40·9 w | — | R2 |
| 33·9 | — | Q3 |
| 31·6 | | |
| 28·2 | — | P3 |
| 24·6 | — | P4 |
| 19·1 sd | — | P6 |
| 13·4 | — | P7, 8 |
| 07·1 | — | P9 |
| 03·2 | — | P10 |
| 44,699·0 | | |
| 93·9 | — | P12 |
| 85·4 ss | $A_3$ | ~R8 |
| 80·4 | — | R2 |
| 73·0 ss | — | Q1—3 |
| 69·3 s | | |
| 65·7 d | | |
| 60·0 d | | |
| 58·0 d | ($c_1$) | |
| 56·1 w | — | P7 |
| 49·6 | — | P8 |
| 45·5 w | — | P9 |
| 41·2 | — | P10 |
| 37·5 | — | P11 |
| 32·6 | — | P12 |
| 27·5 | | |
| 21·4 wd | | |
| 18·0 | | |
| 12·5 | | |
| 10·3 | | |
| 04·4 | | |
| 00·0 | | |
| 44,597·2 | | |
| 90·6 | | |
| 86·5 wd | | |
| 83·0 | | |
| 75·4 wd | | |
| 67·7 s | $h_2$ | R-head |
| 58·3 w | | |
| 54·7 s | | |
| 52·4 w | | |
| 48·4 w | | |
| 39·2 w | | |
| 44,494·8 ss | $F_4$ | R-head |
| 80·1 s | — | Q-head |
| 75·8 | | |
| 70·4 | | |
| 65·6 | | |
| 59·3 | $e_2$ | R-head |
| 49·8 | | |
| 43·8 s | — | Q-head |
| 41·6 s | | |
| 38·1 | | |
| 33·1 s | | |
| 29·5 | | |
| 26·2 s | | |
| 22·9 w | | |
| 19·2 w | | |
| 14·6 | | |
| 10·3 s | $J_4$? | R-head |
| 06·2 | | |
| 01·7 | | |
| 44,396·1 | | |
| 90·5 d | | |
| 85·7 w | | |
| 81·6 | | |
| 43·7 s | $D_2$ | ~R10 |
| 38·8 w | | |
| 05·8 ss | $C_2$ | ~R13 |
| 04·8 | — | R9 |
| 01·7 | — | R5 |
| 44,298·1 | — | R3 |
| 94·4 | — | R1 |
| 88·6 s | — | Q1—3 |
| 86·3 | — | Q5 |
| 82·9 | — | Q7 |
| 78·6 | — | Q9 |
| 76·6 w | — | P5 |
| 73·3 s | — | Q11 |
| 70·3 w | — | P7; Q12 |
| 66·7 s | — | Q13; P8 |
| 63·2 | — | P9; Q14 |
| 59·4 | — | Q15; P10 |
| 55·7 | — | P11; Q16 |
| 50·8 | — | Q17; P12 |
| 47·2 | — | P13 |
| 42·9 | — | P14 |

TABLE 29.—*Continued.*

| Frequency | Assignment Band | Lines |
|---|---|---|
| 39·4 | — | Q19 |
| 34·5 wd | | |
| 29·4 sd | — | Q21 |
| 24·3 wd | | |
| 18·5 | — | Q23 |
| 13·5 wd | | |
| 06·4 ss | $H_3$ | R-head |
| 02·5 | | |
| 44,195·8 | | |
| 91·0 s | — | Q-head |
| 87·7 s | | |
| 86·0 w | | |
| 83·6 s | | |
| 81·6 w | | |
| 78·8 s | | |
| 76·4 ww | | |
| 73·4 s | | |
| 70·2 | | |
| 66·6 | | |
| 57·6 d | | |
| 52·6 d | | |
| 48·5 | | |
| 42·7 w | | |
| 44,085·4 ss | $E_3$ | R-head |
| 81·3 ss | $b_1$ | R-head |
| 75·2 w | | |
| 68·2 s | — | Q-head |
| 66·5 | | |
| 63·3 d | | |
| 60·3 | | |
| 58·7 | | |
| 54·9 | | |
| 52·7 | | |
| 50·3 | | |
| 45·6 s | | |
| 40·9 w | | |
| 36·2 s | | |
| 30·8 w | | |
| 27·1 s | $a_1$ | R-head |
| 22·8 w | | |
| 17·7 s | | |
| 15·3 | | |
| 13·6 | | |
| 08·6 | | |
| 06·1 | | |
| 02·5 | | |
| 00·0 | | |
| 43,996·8 | | |
| 94·9 | | |
| 88·9 w | | |
| 85·3 s | | |
| 81·2 wd | | |
| 75·9 s | | |
| 73·0 | | |
| 70·1 | | |
| 65·6 s | | |
| 59·1 sd | | |
| 53·7 | | |
| 43,872·9 ss | $f_2$ | R-head |
| 69·3 | | |
| 60·1 sd | — | Q-head |
| 48·7 | | |
| 44·6 | | |
| 41·0 | | |
| 36·8 | | |
| 33·5 | | |
| 28·4 | | |
| 17·5 s | $J_3$ | R-head |
| 14·2 | | |
| 05·9 | | |

| Frequency | Assignment Band | Lines |
|---|---|---|
| 00·9 ss | $G_3$ | |
| 43,797·5 ss | | |
| 93·2 | | |
| 90·0 | | |
| 86·8 d | | |
| 80·1 | | |
| 72·6 s | | |
| 31·2 ss | $B_2$ | R10 |
| 17·1 s | — | Q2—4 |
| 14·8 | — | Q5, 6 |
| 11·8 | — | Q8; P3 |
| 08·0 d | — | Q10; P4, 5 |
| 02·5 s | — | Q12; P6 |
| 43,697·0 | — | P7 |
| 94·4 | — | P8 |
| 90·7 | — | P9 |
| 86·9 s | — | P10 |
| 82·8 | — | P11 |
| 77·4 w | — | P12 |
| 74·2 ss | $A_2$ | ~R9 |
| 68·7 | — | R2 |
| 60·4 sd | — | Q3—5 |
| 57·9 | — | Q7; P2 |
| 54·1 s | — | Q9; P3 |
| 52·6 w | — | P4 |
| 49·7 | — | Q10; P5 |
| 46·5 s | — | P6; Q11 |
| 44·7 w | — | P7; Q12 |
| 38·2 s | — | P8 |
| 34·4 | — | P9 |
| 30·2 s | — | P10 |
| 26·3 | — | P11 |
| 21·4 | — | P12 |
| 10·5 | — | P14 |
| 43,530·7 s | | |
| 25·5 ss | $h_1$ | R-head |
| 03·7 ss | $F_3$ | ~R8 |
| 43,489·8 s | — | Q2, 3 |
| 88·1 sd | — | Q4—7 |
| 84·6 | — | Q8; P3 |
| 81·9 | — | Q9, 10; P4 |
| 79·3 | — | Q11 |
| 74·6 | — | Q6; P12 |
| 71·6 | — | P7 |
| 67·0 | — | P8 |
| 62·8 | — | P9 |
| 58·9 | — | P10 |
| 54·5 d | — | P11 |
| 49·8 | — | P12 |
| 44·7 | — | P13 |
| 41·4 s | $J_3$ | ~R8 |
| 34·9 w | — | R1 |
| 27·7 ss | $e_1$ | R-head |
| 22·0 | | |
| 17·2 w | | |
| 11·7 s | — | Q-head |
| 05·6 s | | |
| 01·2 w | | |
| 43,397·2 s | | |
| 91·7 | | |
| 87·7 | | |
| 83·0 w | | |
| 77·9 s | | |
| 69·4 | | |
| 64·6 | | |
| 58·9 | | |
| 48·7 | | |
| 37·3 | | |
| 09·2 d | $D_1$ | |
| 43,273·9 ss | $C_1$ | ~R13 |

| Frequency | Assignment Band | Lines |
|---|---|---|
| 69·0 | — | R5 |
| 66·2 w | — | R3 |
| 62·2 w | — | R1 |
| 56·5 s | — | Q1—3 |
| 54·1 | — | Q5 |
| 50·9 s | — | Q7 |
| 46·7 | — | Q9 |
| 44·4 w | — | P5 |
| 41·4 | — | Q11 |
| 38·3 w | — | P7 |
| 35·0 | — | Q13 |
| 31·4 | — | P9 |
| 27·6 | — | Q15 |
| 23·6 | — | P11 |
| 19·4 | — | Q17 |
| 15·5 | — | P13 |
| 12·0 w | | |
| 10·0 w | — | Q19 |
| 06·7 | — | P15 |
| 03·8 | — | Q21 |
| 43,198·1 | — | P17 |
| 93·8 w | | |
| 83·6 ss | $H_2$ | R-head |
| 78·1 | | |
| 73·8 w | | |
| 69·2 s | — | Q-head |
| 67·1 | | |
| 64·1 | | |
| 60·3 | | |
| 58·5 | | |
| 56·1 | | |
| 50·7 s | | |
| 47·7 | | |
| 43·2 | | |
| 29·9 | | |
| 25·5 | | |
| 20·4 | | |
| 11·5 d | | |
| 43,073·8 ss | $E_2$ | ~R13 |
| 69·9 | — | R5 |
| 67·3 | — | R3 |
| 63·4 | — | R2 |
| 56·9 s | — | Q2, 3 |
| 55·2 | | |
| 51·8 | | |
| 48·8 s | — | Q8 |
| 46·9 | — | Q9 |
| 43·6 | — | Q10 |
| 41·6 | — | P6; Q11 |
| 38·5 | — | P7; Q12 |
| 34·5 | — | P8; Q13 |
| 31·7 s | — | P9; Q14 |
| 27·0 | — | P10; Q15 |
| 24·3 | — | P11; Q15 |
| 21·1 | — | P12 |
| 15·3 s | — | P13 |
| 11·4 w | | |
| 06·1 s | | |
| 01·3 w | | |
| 42,995·9 s | $b_0$ | R-head |
| 90·9 | | |
| 84·9 | | |
| 73·2 s | | |
| 70·6 | | |
| 67·2 | | |
| 61·6 d | | |
| 55·5 | | |
| 49·4 sd | $a_0$ | R-head |
| 46·3 | | |
| 38·1 s | | |

TABLE 29.—*Continued.*

| Frequency | Assignment Band | Lines | Frequency | Assignment Band | Lines | Frequency | Assignment Band | Lines |
|---|---|---|---|---|---|---|---|---|
| 29·5 s | | | 31·9 s | — | Q1—3 | 42,398·3 w | — | P7 |
| 26·3 | | | 30·1 s | — | Q5 | 95·3 | — | P8 |
| 20·3 | | | 28·3 s | — | P2; Q7 | 90·1 | — | P9 |
| 13·4 s | | | 23·8 sd | — | P4; Q9 | 87·0 | — | P10 |
| 11·3 | | | 19·8 | — | Q11 | 82·8 | | |
| 09·3 | | | 16·0 s | — | P6 | 77·8 | — | P12 |
| 05·3 | | | 12·1 | — | Q13 | 73·0 | | |
| 02·6 | | | 08·3 s | — | P8 | 66·5 | | |
| 42,799·5 | | | 04·6 | — | Q15 | 61·4 | | |
| 93·7 | | | 00·4 s | — | P10 | 54·6 | | |
| 89·6 w | | | 42,591·2 | — | Q19; P12 | 48·9 | | |
| 87·0 s | | | 87·3 d | | | 44·0 | | |
| 80·2 w | | | 80·5 | — | Q21 | 42,225·5 ss | $C_0$ | ~R13 |
| 74·9 | | | 77·1 | | | 20·9 | — | R5 |
| 71·3 | | | 69·3 | — | Q23 | 17·5 | — | R3 |
| 67·4 | | | 63·5 | | | 07·8 sd | — | Q1—3 |
| 61·4 | $G_1$ | | 56·7 | | | 02·5 s | — | Q7 |
| 56·5 | | | 42,488·3 ss | $F_2$ | ~R10 | 42,198·6 s | — | Q9 |
| 49·9 w | | | 74·0 s | — | Q2, 3 | 96·0 w | — | P5 |
| 42·4 | | | 72·2 s | — | Q4, 5 | 92·9 | — | Q11 |
| 32·2 w | | | 68·9 | — | Q7 | 90·2 | — | P7 |
| 13·5 s | | | 66·5 | — | Q9 | 87·0 | — | Q13 |
| 08·7 s | | | 63·6 | — | Q10 | 83·4 | — | P9 |
| 42,679·1 ss | $B_1$ | ~R8 | 58·9 | — | P6; Q12 | 79·1 | — | Q15 |
| 90·8 | — | R2 | 55·9 | — | P7 | 75·3 | — | P11 |
| 82·7 sd | — | Q2, 3 | 51·6 | — | P8 | 71·9 s | — | Q17 |
| 80·6 d | — | Q4, 5 | 47·5 s | — | P9 | 66·8 | — | P13 |
| 77·6 d | — | Q7, 8; P3 | 43·3 | — | P10 | 63·1 d | — | Q19 |
| 73·5 s | — | P4; Q10 | 38·8 | — | P11 | 57·5 s | | |
| 68·3 | — | P6 | 31·1 ss | $J_2$ | ~R9 | 43·8 s | $H_1$ | R-head |
| 63·0 s | — | P7 | 24·2 | — | R2 | 38·5 | | |
| 60·3 w | — | P8 | 18·0 s | — | Q1, 3 | 33·5 | | |
| 56·8 ss | — | P9 | 14·8 | — | P2; Q7 | 28·4 s | — | Q-head |
| 52·9 | — | P10 | 11·3 | — | P3; Q8 | 25·4 d | | |
| 48·4 w | — | P11 | 07·0 | | | 21·5 | | |
| 44·5 ss | $A_1$ | ~R9 | 02·3 | — | P6 | 10·8 | | |
| 39·6 | — | R2 | | | | | | |

TABLE 30. *Additional frequencies (cm.$^{-1}$) of absorption maxima in acetylene at 200°.*

| Frequency | Assignment Band | Lines | Frequency | Assignment Band | Lines | Frequency | Assignment Band | Lines |
|---|---|---|---|---|---|---|---|---|
| 42,341·2 s | $J_2$ continuation | | 35·8 ss | — | R-head | 51·2 ss | | |
| 37·2 | | | 30·7 | | | 44·1 ss | $H_1$ | R-head |
| 34·8 | | | 25·8 | | | 37·6 | | |
| 28·4 | | | 22·3 s | | | 32·3 | | |
| 27·5 | | | 21·0 | | | 28·6 s | — | Q-head |
| 25·6 | | | 18·6 | | | 23·8 | | |
| 20·5 | | | 16·5 | | | 20·6 | | |
| 17·5 | | | 14·1 | | | 19·4 | | |
| 12·1 | | | 11·1 | | | 13·2 | | |
| 09·1 | | | 06·3 | | | 08·2 | | |
| 00·6 | | | 04·1 | | | 02·7 | | |
| 42,295·4 | | | 42,198·9 | | | 42,097·0 | | |
| 91·8 | | | 94·9 | | | 91·4 | | |
| 89·9 | | | 90·8 | | | 85·8 | | |
| 86·2 | | | 88·1 | | | 81·1 d | | |
| 81·7 | | | 86·2 | | | 75·8 w | | |
| 70·2 ss | $k_1$ | R-head | 82·5 | | | 72·8 | | |
| 65·1 w | | | 71·8 ss | $I_1$ | R-head | 66·8 | | |
| 56·4 w | | | 67·9 w | | | 58·7 | | |
| 50·8 ss | | | 62·0 w | | | 52·6 | | |
| 46·3 | | | 57·6 | | | 42·9 ss | $E_1$ | R-head |
| 42·3 | | | 53·9 | | | 39·1 | | |

TABLE 30.—*Continued.*

| Frequency | Assignment Band | Lines |
|---|---|---|
| 36·8 | | |
| 32·6 | | |
| 26·0 s | — | Q-head |
| 24·2 | | |
| 20·6 | | |
| 16·0 | | |
| 13·4 | | |
| 11·0 | | |
| 07·4 s | | |
| 04·0 | | |
| 01·0 d | | |
| 41,995·9 | | |
| 92·9 | | |
| 91·5 | | |
| 88·1 w | | |
| 84·4 s | | |
| 79·6 w | | |
| 75·5 s | | |
| 71·2 | | |
| 65·8 | | |
| 60·7 | | |
| 55·0 s | | |
| 48·9 wd | | |
| 42·9 | | |
| 36·9 | | |
| 33·0 | | |
| 28·3 ss | $K_2$ | R-head |
| 24·4 | | |
| 16·4 | | |
| 10·0 s | — | Q-head |
| 08·3 | | |
| 05·1 | | |
| 03·1 | | |
| 00·4 | | |
| 41,897·3 | | |
| 94·0 | | |
| 88·2 | | |
| 83·3 | | |
| 79·5 | | |
| 74·5 | | |
| 70·1 | | |
| 64·4 | | |
| 58·5 wd | | |
| 53·4 s | | |
| 47·2 d | | |
| 41·6 s | | |
| 38·1 | | |
| 35·1 | | |
| 31·0 | | |
| 28·7 | | |
| 24·6 | | |
| 17·7 ss | $L_2$ | ~R13 |
| 16·1 | | |
| 08·7 | — | R2 |
| 01·3 | — | Q2, 3 |
| 41,739·9 | — | Q4 |
| 96·6 | — | Q6 |
| 93·4 | — | Q8 |
| 91·7 | — | P4; Q9 |
| 88·1 s | — | P5; Q10 |
| 85·5 | — | P6; Q11 |
| 82·4 s | — | P7; Q12 |
| 78·7 | — | P8; Q13 |
| 75·8 | — | P9; Q14 |
| 72·0 | — | P10; Q15 |
| 68·9 s | — | P11; Q16 |
| 65·9 s | | |
| 59·2 | | |
| 56·2 | | |
| 49·5 s | | |

| Frequency | Assignment Band | Lines |
|---|---|---|
| 44·8 w | | |
| 39·2 s | | |
| 33·4 w | | |
| 26·8 sd | | |
| 21·3 | | |
| 15·5 | | |
| 08·6 | | |
| 06·9 | | |
| 02·3 d | | |
| 41,694·5 | | |
| 91·0 | | |
| 88·0 | | |
| 78·4 | | |
| 70·3 s | | |
| 64·3 s | | |
| 56·8 | | |
| 49·7 | | |
| 46·3 | | |
| 10·6 ss | $B_0$ | R-head |
| 06·8 | | |
| 41,596·2 s | — | Q-head |
| 91·8 | | |
| 87·9 | | |
| 85·1 | | |
| 82·8 | | |
| 80·5 | | |
| 77·6 | | |
| 70·4 ss | $A_0$? | R-head |
| 66·6 | | |
| 61·1 | | |
| 56·4 | | |
| 49·4 s | — | Q-head |
| 46·2 | | |
| 19·2 s | | |
| 13·4 | | |
| 03·8 s | | |
| 41,499·8 s | | |
| 91·4 | | |
| 88·5 | | |
| 83·8 | | |
| 79·3 | | |
| 74·2 | | |
| 68·4 | | |
| 63·0 | | |
| 53·7 ss | $F_1$ | R-head |
| 50·9 | | |
| 46·4 | | |
| 40·2 s | — | Q-head |
| 37·9 | | |
| 34·7 | | |
| 32·1 | | |
| 29·2 | | |
| 24·7 | | |
| 17·2 | | |
| 09·7 | | |
| 01·5 ss | $J_1$ | R-head |
| 41,395·6 | | |
| 89·4 ss | — | Q-head |
| 87·8 | | |
| 85·5 | | |
| 81·3 | | |
| 77·2 | | |
| 72·8 s | | |
| 68·1 | | |
| 65·3 | | |
| 61·6 | | |
| 52·6 | | |
| 48·4 | | |
| 42·6 | | |
| 36·6 | | |

| Frequency | Assignment Band | Lines |
|---|---|---|
| 31·7 | | |
| 25·0 | | |
| 20·8 | | |
| 14·9 | | |
| 11·4 | | |
| 03·8 | | |
| 41,220·0 ss | $M_2$ | ~R10 |
| 15·5 | | |
| 07·7 s | — | Q-head |
| 04·7 | | |
| 00·9 | | |
| 41,198·5 | | |
| 95·1 | — | P5; Q10, 11 |
| 90·0 | — | Q12 |
| 88·9 | — | P6 |
| 83·2 | — | P8 |
| 75·5 | — | P10 |
| 69·7 | — | P11 |
| 63·0 ss | $N_2$ | R-head |
| 59·8 | | |
| 55·7 w | | |
| 50·7 sd | — | Q-head |
| 47·1 | | |
| 43·6 | | |
| 39·1 | | |
| 35·2 | | |
| 30·5 | | |
| 26·5 | | |
| 22·8 | | |
| 18·7 | | |
| 13·5 | | |
| 08·9 | | |
| 04·4 | | |
| 41,096·5 s | $H_0$ | R-head |
| 92·1 | | |
| 88·2 | | |
| 85·5 s | | |
| 40,994·4 s | $E_0$ | R-head |
| 90·3 | | |
| 77·5 s | — | Q-head |
| 08·6 | | |
| 40,888·6 ss | $K_1$ | R-head |
| 85·2 | | |
| 75·8 | | |
| 71·0 s | — | Q-head |
| 68·7 | | |
| 65·8 | | |
| 63·1 | | |
| 60·3 | | |
| 40,786·8 s | $L_1$ | R-head |
| 84·1 | | |
| 70·9 d | | |
| 68·1 d | | |
| 65·5 | | |
| 62·5 | | |
| 60·8 | | |
| 57·1 | | |
| 51·5 s | | |
| 47·8 w | | |
| 44·5 | | |
| 38·5 | | |
| 36·0 s | | |
| 28·2 s | | |
| 18·6 | | |
| 40,648·3 wd | | |
| 40,599·1 wd | | |
| 41·2 wd | | |
| 37·3 wd | | |
| 20·0 wd | | |

TABLE 31. *Frequencies (cm.$^{-1}$) of absorption maxima of dideuteroacetylene at 20°.*

(The label of each assigned band is placed opposite the frequency of its R-head.)

| Frequency | Band | Frequency | Band | Frequency | Band | Frequency | Band | Frequency | Band |
|---|---|---|---|---|---|---|---|---|---|
| 47,418·8 s | | 31·7 | | 47·1 | | 47·3 s | $t_4$ | 08·6 | |
| 04·1 sd | | 28·7 | | 43·5 | | 32·9 | | 03·8 | |
| 47,375·6 sd | | 24·3 s | | 42·8 | | 27·4 | | 01·2 | |
| 10·5 | | 22·1 | | 39·1 | | 24·9 | | 45,399·1 | |
| 05·1 d | | 18·6 | | 37·0 w | | 16·4 ss | $B_5$ | 95·1 | |
| 47,299·5 | | 14·8 s | | 34·9 | | 06·7 w | | 92·0 | |
| 93·0 s | $q_5$ | 13·2 s | | 30·7 s | | 45,896·4 s | | 88·1 s | |
| 90·4 | | 10·6 | | 28·0 | | 84·9 wd | | 85·9 | |
| 77·9 s | | 07·2 | | 25·8 | | 76·0 s | $A_5$ | 82·9 d | |
| 75·3 s | | 02·6 s | | 23·0 | | 71·9 w | | 72·9 ss | $E_5$ |
| 72·0 w | | 46,898·9 | | 20·6 s | | 64·0 | | 64·2 | |
| 57·0 s | $p_5$ | 91·5 | | 17·2 | | 60·3 s | $e_4$ | 60·4 | |
| 49·2 | | 89·5 | | 14·1 | | 58·7 | | 57·5 d | |
| 46·6 s | | 85·6 s | $c_4$ | 12·2 | | 56·4 | | 52·6 | |
| 44·7 | | 83·8 | | 08·2 | | 51·2 | | 49·1 | |
| 39·1 | | 81·7 | | 06·8 | | 29·6 | | 47·3 | |
| 36·3 s | | 79·6 | | 02·1 | $b_4$ | 26·8 | | 45·1 | |
| 31·2 | | 76·9 | | 46,397·2 ss | $C_5$ | 20·0 s | | 41·8 | |
| 22·6 s | | 73·0 s | | 93·4 | | 45,689·3 dd | | 33·8 d | $j_4$ |
| 20·3 | | 70·3 | | 91·5 | | 69·9 ss | $F_6+q_3$ | 28·8 | $r_2$ |
| 08·0 | | 66·8 | | 88·5 | | 62·7 w | | 26·3 | |
| 02·9 s | $b_5$ | 62·5 | | 85·9 s | | 60·9 | | 24·5 | |
| 47,195·2 | | 59·9 | | 84·9 s | | 58·8 | | 45,255·7 wd | $a_2$ |
| 91·3 | | 56·4 s | | 82·3 | | 54·0 s | | 45,199·2 s | $w_3$ |
| 88·5 | | 52·6 | | 78·4 s | | 50·5 | | 61·1 | |
| 83·0 | | 45·2 s | | 75·1 s | | 48·4 | | 57·8 | $G_4$ |
| 78·6 sd | $C_6$ | 42·6 | | 72·1 | | 45·6 | | 55·0 | |
| 74·7 | | 35·3 sd | | 69·7 | | 43·6 | | 51·8 | |
| 71·9 | | 31·7 | | 65·2 ss | $a_4$ | 41·7 w | | 48·9 | |
| 69·6 | | 19·7 w | | 63·7 | | 35·3 ss | $p_3$ | 45·3 | |
| 64·5 s | $a_5$ | 46,785·4 d | | 61·4 | | 29·1 | | 42·8 s | |
| 61·8 | | 67·9 w | | 58·0 | | 25·7 | | 39·7 | |
| 59·0 | | 64·9 s | | 51·5 | | 23·0 | | 37·0 | |
| 56·8 | | 57·4 | | 46,274·5 s | | 21·3 | | 34·4 | |
| 55·1 | | 54·9 | | 71·2 | | 19·0 s | | 30·4 s | $t_3$ |
| 52·2 d | | 37·8 sd | | 31·1 | | 15·0 | | 25·0 | |
| 47·4 | | 35·8 sd | | 26·2 s | $H_6$ | 11·8 | | 21·3 | |
| 43·2 | | 21·7 | | 18·8 | | 10·2 | | 17·3 | |
| 39·8 | | 19·5 | | 11·5 | | 08·6 | | 13·0 ss | $B_4$ |
| 32·7 s | | 09·9 | | 06·4 wd | | 04·7 | | 02·0 w | |
| 30·0 | | 05·1 | | 46,198·1 | | 02·0 | | 45,095·3 s | |
| 27·2 | | 02·2 s | $A_6$ | 95·2 d | | 45,594·6 sd | $C_4$ | 93·7 | |
| 47,084·8 sd | | 46,694·8 | | 92·5 s | | 89·7 sd | $b_3$ | 91·9 | |
| 44·2 | | 89·5 w | | 90·7 | | 87·7 | | 89·1 | |
| 28·6 s | | 71·6 | | 88·1 | | 84·3 | | 87·2 | |
| 26·6 s | | 61·5 ss | $e_5$ | 84·6 w | | 81·7 sd | | 84·8 | |
| 24·9 | | 55·3 d | | 78·3 s | | 77·3 | | 74·1 ss | $A_4$ |
| 22·0 | | 45·2 | | 71·6 sd | $f_5$ | 73·3 | | 70·7 | |
| 17·6 d | | 42·9 | | 67·9 | | 70·3 w | | 66·2 | |
| 13·0 | | 26·8 | | 54·5 ss | $E_6$ | 68·5 | | 62·8 | |
| 10·8 | | 15·7 | | 52·6 | | 66·2 | | 59·2 | |
| 07·9 | | 05·2 | | 49·7 | | 63·4 | | 50·0 sd | $e_3$ |
| 04·6 | | 46,514·9 w | | 46·0 | | 55·6 ss | $a_3$ | 46·7 | |
| 01·5 | | 13·5 | | 43·1 | | 51·7 | | 44·5 | |
| 46,999·2 | | 11·8 | | 39·5 s | | 48·9 | | 41·1 | |
| 95·2 s | | 09·4 | | 33·8 | | 45·7 | | 44,910·4 d | |
| 91·9 | | 07·3 | | 32·0 | | 43·4 | | 44,885·5 s | $F_5$ |
| 89·5 | | 46,488·5 ss | $q_4$ | 30·0 | | 39·0 s | | 65·5 s | |
| 87·7 | | 83·3 | | 27·8 | | 35·4 | | 64·9 s | |
| 85·1 | | 80·0 | | 25·0 | | 29·9 | | 45·4 sd | $J_5$ |
| 71·8 s | $r_4$ | 76·7 | | 21·4 | | 25·0 | | 39·4 sd | $q_2$ |
| 69·7 | | 72·4 s | | 18·9 | | 22·0 | | 38·2 | |
| 68·0 | | 70·9 s | | 46,087·4 s | $d_3$? | 18·8 s | | 34·4 | |
| 66·3 | | 68·8 | | 74·4 sd | $c_3$ | 02·0 w | | 29·3 w | |
| 63·2 | | 66·6 | | 68·5 w | | 45,479·2 d | | 25·8 d | |
| 60·2 | | 64·3 | | 43·7 | | 69·5 | | 06·4 s | $p_2$ |
| 56·6 | | 61·0 | | 19·6 sd | $w_4$ | 58·0 s | $H_5$ | 05·1 | |
| 52·0 s | | 60·0 | | 45,997·3 | | 51·8 s | | 01·3 | |
| 46·1 sd | | 55·3 | | 95·0 | | 37·9 d | | 44,797·2 | |
| 43·6 | | 51·4 ss | $p_4$ | 71·3 d | $G_5$ | 20·3 s | $y_4$ | 94·3 | |
| 34·6 | | 49·9 | | 62·0 d | | 13·7 | | 90·4 | |

TABLE 31.—*Continued.*

| Frequency | Band | Frequency | Band | Frequency | Band | Frequency | Band | Frequency | Band |
|---|---|---|---|---|---|---|---|---|---|
| 88·2 | | 85·7 | | 44,366·7 wd | | 62·1 wd | | 46·5 d | |
| 80·2 s | $C_3$ | 83·2 | | 22·4 wd | | 43·5 s | $J_4$ | 43·4 | |
| 77·0 | | 79·9 w | | 16·0 wd | | 43,998·0 | | 38·2 s | $f_2$ |
| 75·3 | | 71·3 ss | $E_4$ | 01·2 s | $t_2$ | 66·7 w | | 06·1 wd | $j_3$ |
| 69·8 sd | $b_2$ | 59·0 | | 44,296·7 ss | $B_3$ | 56·4 | $C_2$ | 43,610·4 w | |
| 37·0 s | $a_2$ | 57·9 | | 81·1 s | | 43,846·9 wd | | 43,535·0 w | |
| 34·1 | | 53·9 d | | 60·2 ss | $A_3$ | 28·1 s | $H_3$ | 43,471·3 s | $B_2$ |
| 44,661·8 dd | | 50·6 d | | 57·2 | | 08·6 s | $u_2$ | 60·8 d | |
| 46·3 s | $H_4$ | 48·0 | | 52·5 w | | 43,781·6 d | | 37·2 s | $A_2$ |
| 39·2 s | $u_3$ | 43·2 s | | 49·5 w | | 75·5 d | $y_2$ | 33·8 | |
| 21·8 wd | | 39·3 | | 31·8 d | $e_2$ | 71·7 d | | 43,373·6 | |
| 04·1 sd | $y_3$ | 36·8 | | 44,194·9 w | | 68·3 | | 43,284·0 wd | |
| 44,598·7 | | 31·4 | | 63·7 | | 65·5 w | | 66·1 s | $F_3$ |
| 96·3 | | 24·3 s | $j_3$ | 44,094·6 w | | 56·7 ss | $E_3$ | 48·9 | |
| 93·1 w | | 44,416·0 wd | | 82·1 s | $F_4$ | 54·9 | | 29·9 s | $J_3$ |
| 89·7 | | | | | | | | | |

TABLE 32. *Additional frequencies (cm.$^{-1}$) of absorption maxima in dideuteroacetylene at 200°.*

(The label of each assigned band is placed opposite the frequency of its R-head.)

| Frequency | Band | Frequency | Band | Frequency | Band | Frequency | Band | Frequency | Band |
|---|---|---|---|---|---|---|---|---|---|
| 43,196·6 wd | | 06·2 d | | 42,888·7 d | | 34·0 | | 42,439·8 ss | $F_2$ |
| 77·1 wd | | 42,993·3 | | 66·0 | | 20·3 ss | | 24·8 s | |
| 54·4 wd | | 90·6 | | 19·2 d | | 12·1 | | 06·0 s | $J_2$ |
| 15·0 wd | | 66·7 s | | 42,791·6 s | | 06·9 | | 03·3 | |
| 43,087·2 d | | 55·8 s | | 69·2 | | 03·2 | | 42,398·5 | |
| 43·0 s | | 44·2 wd | | 56·5 | | 42,564·7 wd | | 57·6 | |
| 24·6 | | 32·7 ssd | $E_2$ | 44·5 | | 41·0 | | 32·6 | |

The above results have been considerably enriched by the loan to us by Dr. W. C. Price of his multiple reflexion cell, and by the supply of special-quality carbide from Mr. W. P. Phillips. In the theoretical analysis, Professor D. P. Craig acted as our constant mentor and guide. We had helpful discussions also with Professor R. Mecke and with Dr. G. Herzberg, who in association with Dr. K. K. Innes is conducting high-resolution work on some of the bands.

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## 554. *Ultra-violet Absorption Spectra of* trans- *and* cis-*Stilbenes and Their Derivatives. Part I.* trans- *and* cis-*Stilbenes.*

By R. N. BEALE and E. M. F. ROE.

The ultra-violet absorption spectra of solutions of *trans*- and *cis*-stilbene have been measured at room temperature and of *trans*-stilbene at −130°. The results for *trans*-stilbene have been compared with recent semi-theoretical calculations of ν- and *f*-values, which employ LCAO MO methods or the free-electron model or regard the molecule as a system of coupled harmonic oscillators. This comparison reveals that good prediction of ν may be achieved, while predicted *f*-values deviate by amounts up to 100% from the observed figure. Possible explanations are given for the considerable spectral changes in *trans*-stilbene on refrigeration.

EARLIER investigations of certain basic derivatives of *trans*-stilbene, some of which are tumour-inhibitory and carcinogenic, revealed a correlation between biological effects and molecular shape, the latter property being reflected in the near-ultra-violet absorption spectra of the compounds considered (Haddow, Harris, Kon, and Roe, *Phil. Trans., A*, 1948, **241**, 147; see also Beale and Roe, *J. Amer. Chem. Soc.*, 1952, **74**, 2302). In order

to classify in greater detail the effects of the type and position of substitution on the frequency and intensity of this absorption, a larger series of stilbene derivatives has been examined. For an interpretation of their spectra, an understanding of the mechanism of ultra-violet absorption in *trans*- and *cis*-stilbene is of fundamental importance and our first study is concerned therefore with the experimental results for these two compounds and with a discussion of theoretical predictions and interpretations of the spectroscopic data.

*Ultra-violet Absorption in* trans-*Stilbene.*—Since the earliest published spectrum of *trans*-stilbene (Baly and Tuck, *J.*, 1908, **93**, 1909) interpretation of its near-ultra-violet absorption bands in terms of the chromophores responsible for absorption has been attempted by a number of investigators. Among these, Stobbe and Ebert (*Ber.*, 1911, **44**, 1289) noted the stronger, lower-frequency absorption in stilbene and tolane compared with diphenylmethane. Ley (*Ber.*, 1917, **50**, 243; 1918, **51**, 1817), who had observed the changes in frequency and extinction which occur with substitution at the stilbene α-carbon atom, attributed the long-wave-length band first (*loc. cit.*, 1917) to the ·C=C· chromophore and later (1918) to a chromophore comprising either the complete molecule or the styrene portion thereof. Arends (*Ber.*, 1931, **64**, 1936), comparing the spectra of stilbene and styrene, assigned the stilbene long-wave-length band at 294 mμ to the Ph·C=C· chromophore which in styrene gives rise to the band at 244 mμ. The 210-mμ stilbene band he attributed to the benzene chromophore, but neglected to assign the band in the 226-mμ region. The measurements by Smakula and Wasserman (*Z. physikal. Chem.*, 1931, **155**, *A*, 353) and Smakula (*ibid.*, 1934, **25**, *B*, 90) indicated the presence of vibrational fine structure in *trans*-stilbene's long-wave-length band, and this, together with Hausser's data (*Z. tech. Physik*, 1934, **15**, 10) on fine-structure frequency differences in the higher diphenylpolyenes (where these differences, of the order of 1500 cm.$^{-1}$, were correlated with the Raman frequency of 1600 cm.$^{-1}$), was regarded as evidence that this band is due to an excitation involving the ethylenic double bond.

*Recent Experimental and Theoretical Work.*—More recent semi-theoretical investigations of the spectra of stilbene and related polyenes have been concerned with the prediction of band frequencies and intensities (Mulliken and Rieke, *Rept. Progr. Phys.*, 1941, **8**, 231; Bayliss, *J. Chem. Phys.*, 1948, **16**, 287; W. Kuhn, *Helv. Chim. Acta*, 1948, **31**, 1780; H. Kuhn, *J. Chem. Phys.*, 1949, **17**, 1198; Dewar, *J.*, 1952, 3544). It is of interest to compare these values with the experimental data, and since the detail reported in the literature for the spectra of *trans*- and *cis*-stilbene varies considerably, both high- and low-wave-length bands have been re-examined. Our experimental results are shown in the Figure.

The broad high-wave-length band (subsequently called the A-band) in *trans*-stilbene can be further sub-divided into three bands, two with maxima at 307·5 and 295·5 mμ and a third, submerged band at 321 mμ. The low-wave-length band (subsequently called the B-band) is of about half the intensity of A (measured as $f = 4{\cdot}315 \times 10^{-9} \int \varepsilon d\nu$, where $\nu$ is in cm.$^{-1}$ and $\varepsilon$ is the molar extinction coefficient), but it has a closely similar pattern of structure, with submerged bands at 236 * and 222 mμ * and a maximum at 228·5 mμ. The Table summarises these spectral data. Thus, at 20° the A-band structure in *trans*-stilbene shows frequency separations of ~1340 cm.$^{-1}$ (in ethanol, hexane, glycerol, and Perspex solutions) which become 1480 cm.$^{-1}$ at −130° (in mixed alcohols). The differences between these values may not be significant, since broadening and overlap of vibrational peaks at room temperatures would tend, in any case, to reduce their frequency intervals. In the B-band at 20° the frequency separations are also ~1340 cm.$^{-1}$ (in ethanol, hexane, and glycerol); for technical reasons (see Experimental section) a value at low temperatures could not be obtained. Comparison with the most recently published spectrum of *trans*-stilbene (Calvin and Alter, *J. Chem. Phys.*, 1951, **19**, 765; A-band only) at room temperature in ethanol solution shows agreement for the extinction of the 295·5-mμ maximum; Calvin and Alter's measurements were made at larger wave-length intervals and so revealed a shoulder rather than a maximum at 307·5 mμ. This is also the case in Smakula and Wasserman's curve (*loc. cit.*) where extinction values (corrected for their definition of

* See note in Table.

extinction coefficient by a factor $1/2{\cdot}3 \times 10^3$) are ~7% lower than those reported here for both A- and B-bands, owing probably to a difference in concentration (or some other experimental detail) rather than to isomerisation, which changes the extinctions of A- and B-bands in opposite directions.

*Ultra-violet absorption spectra of* trans- *and* cis-*stilbene.*

| | | A-band | | B-band | | |
|---|---|---|---|---|---|---|
| Compound | Temp. | $\lambda_{max.}$ (mμ) | ε | $\lambda_{max.}$ (mμ) | ε | Solvent |
| *trans*-Stilbene ..... | ~20° | (321) * | (~17,600) | (236) | (~11,100) | 95% EtOH |
| | | 307·5 | 28,300 | 228·5 | 16,400 | |
| | | 295·5 | 29,000 | (222) | (~14,900) | |
| *trans*-Stilbene ..... | ~20 | (320) | (~16,600) | (236) | (~11,000) | Hexane |
| | | 307 | 27,300 | 228·5 | 17,200 | |
| | | 294 | 29,100 | (222) | (~16,000) | |
| *trans*-Stilbene ..... | −130 | 326·2 | 25,000 | — | — | Mixed alcohols † |
| | | 311·2 | 38,500 | | | |
| | | 297·5 | 22,500 | | | |
| *cis*-Stilbene ..... | ~20 | 280 | 10,450 | 224 | 24,400 | 100% EtOH |

* Figures in parentheses denote the estimated maxima of submerged bands.
† Mixture of 80% EtOH, 10% MeOH, and 10% PrⁱOH.

From these results, it is reasonable to conclude, with Smakula and Hausser and their colleagues, that the vibrational fine structure in the A-band originates in an ethylenic C=C stretching frequency. The results of Coulson and Jacobs (*J.*, 1949, 1983) show that the C=C bond undergoes the largest change in bond-order on excitation of the molecule, and thus the greatest change in amplitude of vibration. As a result the A-band fine structure should show the C=C vibrational frequency more strongly than any other. The similar pattern of fine structure and the same approximate Δν-value in the B-band suggest the same origin for the fine structure also. The detailed characteristics of this band will be discussed in a later publication.

The experimental data may now be compared with recent predicted *f*- and ν-values for the A-band, and it may be noted that Ley's suggestion (*loc. cit.*, 1918) that this band originates in an electronic transition involving the complete molecule is supported by this recent work. In Mulliken and Rieke's investigations (*loc. cit.*) conventional LCAO MO theory was used and the equation derived for the intensity of an absorption band in terms of oscillator strength *f* was :

$$f = 1{\cdot}085 \times 10^{11}\nu D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $D$ is the dipole strength of a transition between two electronic states with orbital wave functions $\psi_k$ and $\psi_l$. Further :

$$D = GQ^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$Q = \int \psi_k (\Sigma_i r_i) \psi_l \mathrm{d}\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and $G$ is a numerical factor to allow for degeneracy of levels; $r_i$ is the radius vector of the $i$th electron referred to real co-ordinate axes fixed in the molecule. These authors showed that *trans*-stilbene's A-band, due to an N–V transition (Mulliken, *J. Chem. Phys.*, 1939, **7**, **14** *et seq.*), should be the strongest of their four calculated transitions and contain the major part of the spectral intensity. Their semi-theoretical *f*-value for the band is 0·55 (a correction factor * of 0·34 is used for this molecule). The authors compare this figure with their value calculated from the experimental data of Lewis, Magel, and Lipkin (*J. Amer. Chem. Soc.*, 1940, **62**, 2973), and the resulting $f = 0{\cdot}67$ is in good agreement with semi-theoretical computation. These experimental data are obtained, however, at −90° (*iso*octane solution), under which condition the extinction and *f*-value are reduced below those at room temperature, as shown later in this discussion.

* Such a factor has been shown recently (Coulson *et al.*, *Proc. Roy. Soc.*, 1951, *A*, **206**, 287, 297) to be necessitated by neglect of configuration interaction in simple MO theory, and when this is included much better agreement between theory and experiment is obtained; *e.g.*, for butadiene, $f_{theor.} = 0{\cdot}6$, and $f_{calc.} = 0{\cdot}53$. Configuration interaction is even more important in LCAO predictions for "round-field" molecules such as benzene, coronene, etc., than for "long-field" polyenes, styrene, etc. (Platt, *J. Chem. Phys.* 1950, **18**, 1168).

Bayliss's calculation (*loc. cit.*), on the other hand, assumed for the conjugated polyenes a metallic model in which the π-electrons are " 100% mobile " and subject to a potential-energy field due to the chain of –CH= groups; *i.e.*, the problem was treated as that of an electron gas in a field of uniform potential. This leads to the equation :

$$f \simeq 0{\cdot}134(2N + 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $N$ is the number of double bonds in the molecule. For diphenylbutadiene, Bayliss assumes a contribution of one double bond for the two phenyl groups, and if the same assumption be made for *trans*-stilbene the calculated $f$-value is 0·67. With the more usual equivalent of 1·5 double bonds for each phenyl group the calculated $f$-value is 1·21. Frequency calculations, on Bayliss's assumption, depend not only on $N$ but also on $X$, the overall length of the potential field, and are very sensitive to this value. It is difficult to decide a value for $X$; *e.g.*, in the diphenylpolyenes, good agreement with experimental ν-values is found if $X$ is assumed to be considerably shorter than the overall length of the molecule, and if the phenyl groups contribute, as before, only one double bond to the conjugated system. Bayliss himself points out the weaknesses of the method, namely, the difficulty of deciding a value for $X$, and the assumption of a uniform potential field and infinite ionisation energy.

This model has been modified by H. Kuhn (*loc. cit.*) for the case of the polyenes, by placing the π-electrons in a one-dimensional potential field having a sinusoidal periodicity. The maximum wave-length of the long-wave-length system is then given by

$$\lambda_1 = \frac{1{\cdot}23 \times 10^4}{18{\cdot}8\ (2j' + 1)^{-1} + V_0(1 - (2j')^{-1}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $j'$ = number of conjugated double bonds and $V_0$ = amplitude of the sine-shaped potential along the chain, taken as 2 ev for the polyenes. Thus only one experimentally determined parameter is used and this ($V_0$) is chosen arbitrarily to be twice the value obtained experimentally for the anhydro-bases of the symmetrical cyanine dyes. Good agreement with experimental λ-values is found and, by using equation (5) with $j' = 1{\cdot}5$ double bonds for phenyl, the calculated $\lambda_1$ is 320 mμ for stilbene. Kuhn does not discuss the $f$-values of the polyenes.

Reasonable values of the right order for both $f$ and λ in polyenes have been obtained by W. Kuhn (*loc. cit.*) who regards such linear molecules as systems of coupled harmonic oscillators in a variable potential field. Energy levels were obtained into which were fitted all the π-electrons of the system. The method was more satisfactory than that of Lewis and Calvin (*Chem. Reviews*, 1939, **25**, 273) who took the lowest level of an imaginary harmonic oscillator as the ground state and the first excited level as a molecularly excited state and so treated the molecule as having but one mobile electron. From Kuhn's calculations, the value for the coupling coefficients is so large that an increase of 10% would lead to free mobility of electrons along the chain, as is assumed in Bayliss's model. The following semi-theoretical expressions are derived :

$$\lambda_1 = \lambda_0/\sqrt{1 - 2\alpha \cos[\pi/(n + 1)]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\lambda_1$ = wave-length of maximum absorption for the longest-wave-length transition of the polyene, $\lambda_0$ = 157 mμ, as for the isolated double bond in ethylene, and $n$ = the number of double bonds in the molecule. The constant α cannot be determined theoretically, but is calculated from the experimental data for the polyene with $n = 14$ and $\lambda_1 = 500$ mμ. Then α is found to be 0·461. Again, for the longest-wave-length band :

$$f_1 = 0{\cdot}811 f_0 n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $f_0 = 0{\cdot}22$, for the corresponding ethylene band at 157 mμ. If one assumes with Kuhn (cf. Hausser, *loc. cit.*, 1934) a value of 1·5 double bonds for phenyl, calculation (equation 6) shows that the longest-wave-length band in *trans*-stilbene should occur at 311·5 mμ. When a recent value for $\lambda_0$, *i.e.*, 163 mμ (Platt, Klevens, and Price, *J. Chem. Phys.*, 1949, **17**, 466), is used the predicted $\lambda_1$ for *trans*-stilbene becomes 319 mμ. Strictly, comparison should be made between calculated and observed values for the O–O band of

the long-wave-length transition. In fact, Kuhn's parameter $\alpha$ is obtained by the use of the experimental datum $\lambda_1 = 500$ mμ for the polyene with $n = 14$, and this wave-length corresponds with the longest-wave-length vibrational peak in the spectrum (corrected for solvent shift from hexane to benzene from the data of Hausser *et al.*, *Z. physikal. Chem.*, 1935, **29**, *B*, 442), and not with that of the centre of the system. The author is using, therefore, to obtain one parameter, a wave-length very near the O–O line, and in his comparison of calculated $\lambda_1$-values [from (6)] with the observed data he has referred, again, to the longest-wave-length vibrational bands in the spectra of a number of substituted polyenes showing fine structure. The O–O line in *trans*-stilbene would be that included in the shoulder at 321 mμ at room temperatures and in the separated band at 326 mμ at −130°. More accurately it will be at some wave-length longer than this if the contribution of low-energy molecular deformations could be eliminated (Mulliken, *J. Chem. Phys.*, 1939, **7**, 372). Since the O–O line should be located between the first absorption peak and the first fluorescence peak in the polyenes and the " tails " of these bands overlap in *trans*-stilbene, the O–O transition is found by inspection to occur at about 330 mμ (data of Hausser *et al.*, *loc. cit.*, 1935, pp. 397, 435). Application of Brodersen and Langseth's analysis * to our data (Fig. 1) confirms this; *i.e.*, when $T_2 = 293°$ K the value for *trans*-stilbene's O–O line is 328 mμ, to be compared with that calculated by Kuhn's theory to be 311·5 or 319 mμ, as shown above. For the oscillator strength $f_1$, equation (7) gives a value of 0·71 for *trans*-stilbene, or, by using the $f_0 = 0{\cdot}34 \pm 0{\cdot}15$ of Platt *et al.* (*loc. cit.*), $f_1 = 1{\cdot}1 \pm 0{\cdot}5$. This, together with the corrected value of 0·55 of Mulliken and Rieke, and Bayliss's values of 0·67 or 1·21, may be compared with our experimental *f*-value of 0·755 (at 20°, 95% ethanol as solvent; see Experimental section).

The most recent theoretical treatment of the spectra of polyenes is that by Dewar (*loc. cit.*) who uses a first approximation of the LCAO MO method. By assuming that the double and single bonds require different resonance integrals but that all bonds of one type are equivalent, an equation is derived for the maximum wave-length of the first strong series of bands (neglecting fine structure where this exists) :

$$\lambda_0 = D(1 - a^{-2N-2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $a =$ an empirically determined parameter ($= 2^{\frac{1}{2}} \simeq 1{\cdot}09$) and $D =$ a constant, involving a value for the C–C resonance integral. If a $C–C_{aromatic}$ resonance integral is taken, then $\lambda_0 = 311$ mμ for stilbene, a value not far from the 320 mμ of H. Kuhn and 311·5 or 319 mμ of W. Kuhn. When $D$ is chosen to give good agreement between theory and experiment for butadiene and involves a $C–C_{polyene}$ resonance integral, the predicted $\lambda_0$ is 256 mμ, in poor agreement with experiment. Thus, it appears possible by three different methods to achieve reasonably good semi-theoretical prediction of the λ-value for *trans*-stilbene, while similarly predicted *f*-values deviate by amounts up to 100% from the observed figure.

*The Effect of Low Temperatures on the Spectrum of* trans-*Stilbene.*—It is evident from the Figure that considerable changes in the spectrum of *trans*-stilbene are brought about by refrigeration to −130°. Hausser *et al.* (*loc. cit.*, 1935, p. 391), in their extensive investigations of absorption and fluorescence in substituted polyenes, examined this absorption semi-quantitatively in ethanol–ether at −196°, and in agreement with them we find that the A-band, at low temperature, is much more sharply resolved into its three peaks, called here α, β, and γ, the α-peak occurring at longest wave-lengths. Temperature reduction results also in a small red-shift of about 4 mμ and a marked redistribution of intensity among the vibrational bands. Thus (see Figure) at 20° the intensities of the bands

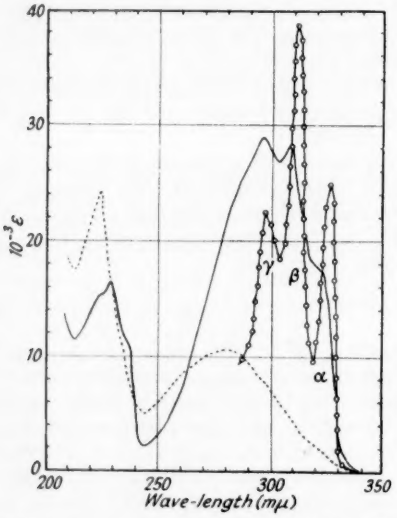
* Brodersen and Langseth (*Kgl. Danske Videnskab. Selsk.*, 1951, **26**, No. 3) have suggested and illustrated the use of changes in absorption with temperature as the basis of a method to localise the O–O line. $\Delta \log \varepsilon$ values are plotted against wave-length or frequency values for the absorption of the pure compound in solution, where $\Delta \log \varepsilon = \log \varepsilon_2 - \log \varepsilon_1$, and $\varepsilon_2$ and $\varepsilon_1$ are molar extinction coefficients taken for the same frequency at temperatures $T_2$ and $T_1$, $T_2$ being greater than $T_1$. A rise in temperature results in an increased number of thermally excited molecules in the solution, leading to increased absorption at frequencies below that of the O–O transition. This increased absorption corresponds to the maximum at lowest frequencies in the $\Delta \log \varepsilon$ $\nu$–$\nu$ curve, and the frequency of the following minimum (rather than that where $\Delta \log \varepsilon = 0$, for reasons discussed in the paper) is identified as the O–O transition.

are in the order $\gamma > \beta > \alpha$, while at $-130°$ this becomes $\beta > \alpha \simeq \gamma$. In spite of increased extinction values for the α- and β-bands, the total *f*-value of the A-system is reduced from 0·755 to ~0·41.

In this connection, Mulliken and Rieke's theoretical consideration (*loc. cit.*) of the effect of temperature on the intensity of an electronic transition is of interest. In equation (3) (p. 2757), the levels $k$ and $l$ are not single each consists of a complicated family of levels, resulting from molecular vibration and rotation and often also electron spin) but, according to these authors, no serious error should be involved if $D$ is defined as the sum total of dipole strengths of all possible transitions from the initial level $l$ to the final level $k$; the distribution of the molecules among the individual initial states should not affect significantly the total $D$ per molecule for a mass of absorbing molecules, and it was noted that the experimental $D$ should be independent of temperature. It may be observed also, since $f = k\int\varepsilon d\nu$ and $f = k'\nu D$ (where $\nu$ is the centre of the band-system), that

$$\int\varepsilon d\nu = k''\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

since $D$ is constant. Thus, if the band does not shift on reduction of the temperature, the integrated area under the band should remain the same; similarly, a bathochromic shift




trans-*Stilbene*, 20° (*in* 95% EtOH), ——
trans-*Stilbene*, −130° (*in mixed alcohols*), –o–o–
cis-*Stilbene*, 20° (*in* 100% EtOH), - - - -

should accompany a reduction in intensity. As shown above, there is an *f*-reduction of ~45% in the *trans*-stilbene A-band at −130°, accompanying a bathochromic shift of only 4 mμ (385 cm.$^{-1}$).

This *f*-reduction is much larger than predicted for such a small shift, so that other factors, as discussed below, must be of great importance. Mulliken and Rieke have noted that deviations from the sum rule for $D$ would be due principally to the fact that the forms of the electronic wave-functions are not quite independent of nuclear positions. Thus, for molecules no longer assumed fixed in their equilibrium configurations the values of $Q$ and $D$ in eqn. (2) will vary somewhat with internuclear distances. It is well known that perturbations due to solvent molecules affect the $\nu$, $f$, and fine structure in absorption bands and their changes with temperature (see, for example, Sheppard *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 2923, 2937; 1944, **66**, 380; Coggeshall and Lang, *ibid.*, 1948, **70**, 3283). It is of interest, therefore, briefly to compare with the *trans*-stilbene measurements the available related data on spectral changes with temperature and those resulting from changing solvents, particularly for non-polar solutes. This is a necessary basis for discussion of the different behaviour of the spectra of basic stilbene derivatives on refrigeration in alcohol solutions and should assist understanding of the changes in *trans*-stilbene's A-band.

Changes in such solvent properties as refractive index and dielectric constant would not be expected to affect considerably the transition dipole of a centrally symmetrical, non-polar solute molecule such as *trans*-stilbene, but the increasing viscosity of the alcohol solutions at lower temperature could make a small contribution to the observed *f*-reduction. Sheppard *et al.* (*loc. cit.*, **1944**) in their discussion of temperature changes in dye spectra suggest that the reduced Brownian movement consequent upon increased viscosity should reduce the uncertainty or spread in energy levels, and Brodersen and Langseth (*loc. cit.*) have shown that if the normal blurring of these levels follows a statistical distribution the standard deviation is of the order of hundreds of wave numbers (~400 cm.$^{-1}$) for a linear conjugated molecule (diphenylbutadiene) at ordinary temperatures. It will be of interest, therefore, to investigate the effects on the A-band *f*-value (and other properties) of solvents more viscous than the alcohols used hitherto, without refrigeration of the solutions.*

An additional result of the sharpening of location of electronic energy levels by this increased viscosity should be greater resolution of vibrational fine structure in the spectrum. However, the main cause of the observed resolution increase is the well-known progressive elimination of higher-energy vibrational and rotational levels by temperature reduction. The lack of this low-temperature resolution in the spectrum reported by Lewis *et al.* (*loc. cit.*) for *trans*-stilbene could be due to the low viscosity of the solution (in *iso*octane) at −90° as well as to the low degree of refrigeration, for their curve shows some changes in extinction values for the main peaks and shoulder.

More than one factor appears to operate to produce the small bathochromic shift of the A-band on refrigeration. Hausser *et al.* (*loc. cit.*) noted that the frequency of absorption in polyenes was proportional to the temperature, and that the ν-change (bathochromic) increased at room temperature with the refractive index of the solvent, as suggested by Kundt's rule (*Ann. Physik*, **1878**, **4**, 34). Thus, some small part of the red shift on refrigeration could be due to the concomitant increase in refractive index of alcohol solutions. Recent theoretical work by Bayliss (*J. Chem. Phys.*, **1950**, **18**, 292) concerning spectral changes on passing from vapour to solution supports this, and suggests, in addition, that such a red shift should be proportional, *inter alia*, to the intensity of the band. This had been confirmed by Coggeshall and Pozefsky (*J. Chem. Phys.*, **1951**, **19**, 980) for the solvent-induced frequency shifts for cata-condensed aromatics and is supported by observations of frequency changes on refrigeration. Thus, like *trans*-stilbene's A-band, the allowed 240—290-mμ transition in naphthalene, having a small *f*-value (0·10),† shows a small red shift (~10 Å) on refrigeration in alcoholic solutions, while the very weak, forbidden, long-wave-length (290—320 mμ) band system in naphthalene ($f = 0{\cdot}002$) † and the similar system at 260 mμ in benzene ($f = 0{\cdot}002$) † undergo no frequency shift with temperature (Mayneord and Roe, *Proc. Roy. Soc.*, 1937, *A*, **158**, 334; Clar, *Spectrochim. Acta*, **1950**, **4**, 116). Further, similarity between the effect of refrigeration and that due to increase in solvent polarity is apparent when comparing the benzene 260-mμ and naphthalene 240—290-mμ systems: the latter shifts bathochromically on passing from *iso*octane to alcohol solutions, while the former is almost independent of solvent (Coggeshall and Lang, *loc. cit.*). The suggestion has been made by the last authors that dipole–dipole interaction between solute and solvent molecules in their excited states could stabilise the excited electronic levels in some systems and produce a red shift, for example, on passing from non-polar to polar solvents. This, again, may play a part in the spectral changes of *trans*-stilbene at low temperatures. It is conceivable that an increased polarity of the refrigerated solvent (due to increased association, cf. Sheppard *et al.*, *loc. cit.*, **1944**) would cause increased polarisation of the solute molecules in their excited states, to which polar structures will make a small but definite contribution which should be negligible in the ground state. If this is so, the low-temperature bathochromic shift should be reduced on using a less polar

* Preliminary measurements in glycerol at room temperatures show a small reduction in *f*-value, a bathochromic shift (possibly due to the high refractive index of the solvent), and redistribution of intensity among the vibrational bands; cf. p. 2762.

† $f = 0{\cdot}10$ for naphthalene's 240—290-mμ transition is calculated by the authors from the data of Mayneord and Roe (*Proc. Roy. Soc.*, 1935, *A*, **152**, 299). *f*-values for the forbidden systems in naphthalene and benzene are from Klevens and Platt (*J. Chem. Phys.*, 1949, **17**, 470) whose value ($f = 0{\cdot}18$) for the naphthalene 240—290-mμ system is in error, owing to incorrect extinction data.

solvent, and might be noted on changing solvents at room temperatures. In fact, in the *iso*octane solution used by Lewis *et al.* there is no bathochromic shift at −90°, although, as already noted, the higher temperature (compared with our measurements) is probably an important factor, and the effect of further refrigeration in a completely non-polar solvent should be tested. At room temperature we have found small differences (5—15 Å) between the $\lambda_{max.}$ values in ethanol and hexane, so this effect may have some small importance in our experiments. Clearly, it should have greater importance in the low-temperature spectra of basic stilbene derivatives, and this appears to be the case (unpublished work).

Redistribution of intensity within the A-band system of *trans*-stilbene is a striking further consequence of temperature reduction. It has been suggested by Professor M. Kasha * that the torsional-potential curves in the ground and excited states of *trans*-stilbene overlap at room temperature, the potential being a maximum for 90° of twist about the double bond in the ground state, and a minimum in the excited state of the molecule (Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265). On refrigeration, fundamental changes are envisaged in the shapes of these curves, with the production of new minima in the excited torsional potential, causing, according to the Franck–Condon principle, redistribution of intensity among the vibrational transitions. An alternative view, for which we are indebted to Professor J. R. Platt, is that at room temperatures some low-wave-length absorption in the A-band results from coupled higher-energy vibrational transitions due to twist of the phenyl rings about the *single* bonds of the bridge. This absorption would be reduced with reduction in probability of twist on increasing the viscosity of the solvent and on refrigeration, clearly altering the relative extinctions of the $\alpha$, $\beta$, and $\gamma$ vibrational bands. It corresponds in position with the A-bands of sterically hindered stilbene derivatives, *e.g.*, 2 : 4 : 6-trimethyl- and 2 : 4 : 6 : 2′ : 4′ : 6′-hexamethyl-stilbene (Haddow *et al.*, *loc. cit.*). Further work at lower wave-lengths and in solvents of varying viscosity and at different temperatures is necessary. The preliminary measurements at room temperatures in glycerol solution show trends in fine structure differences similar to the above, *e.g.*, $\varepsilon_\beta/\varepsilon_\gamma = 1{\cdot}04$, compared with 0·98 in 95% alcohol.

*Ultra-violet Absorption in* cis-*Stilbene.*—The spectrum of *cis*-stilbene in ethanol (see Figure) shows, as in the *trans*-isomer, two main absorption regions; fine structure, however, appears to be missing. The A-band, much less intense, arises at lower wave-lengths ($\lambda_{max.}$ 280 mμ; ε 10,450) than in *trans*-stilbene, while the B-band, increased in intensity, occurs in almost the same region ($\lambda_{max.}$ 224 mμ; ε 24,400) as in *trans*-stilbene. Our data are in good agreement with those of Calvin and Alter (*loc. cit.*) who examined the A-band only, and while there is approximate wave-length agreement with Smakula and Wasserman's curve (*loc. cit.*) their ε value is 30% higher for the A-band and 3% lower for the B-band than reported here, suggestive, with the indications of structure in the A-band, of some *cis–trans*-isomerism during their investigation.

From our Figure, an experimental *f*-value of 0·35 may be calculated for *cis*-stilbene's A-band, to be compared with Mulliken and Rieke's semi-theoretical figure of 0·33 (again with a correction factor of 0·34), calculated without allowance for non-planarity. The reduced intensity of this transition results from at least two effects: (i) the molecule is less extended spatially than that of the *trans*-isomer, so that vector addition of the $r_i$-terms in equation (3) gives a smaller resultant (Mulliken and Rieke, *loc. cit.*; cf. Förster, *Z. Elektrochem.*, 1939, **45**, 548); (ii) steric hindrance to planarity is present, owing to overlap between hydrogen atoms in the phenyl rings, *ortho* to the double bond (Lewis and Calvin, *Chem. Reviews*, *loc. cit.*). The effect of the latter factor on *f*-values has been discussed in connection with sterically hindered *trans*-stilbene derivatives (Beale and Roe, *loc. cit.*).

The absence of fine structure from this A-band, even at −90° (Lewis *et al.*, 1940, *loc. cit.*), has been attributed by these authors to the "loose-bolt effect." Thus, in certain circumstances, the vibrations of low energy of a radical having large mass or low constraint are assumed to couple with the electronic oscillation in such a way that, on excitation,

* Personal communication. A detailed discussion and other aspects of this problem will be published by this author.

there is an abrupt transition from a state in which an electron cloud is oscillating along a single axis to one in which the electronic energy is obliterated and converted into violent atomic vibrational and rotational energies. This will blur the energy levels corresponding to the chief atomic vibrations of high energy and lead to broadening or obliteration of fine structure in the absorption bands. Further, since the process removes the electronic energy of the excited state almost instantaneously, no fluorescence can occur. Lewis *et al.* found no fluorescence in *cis*-stilbene, even at −90° (*iso*octane solution), and their theory was found also to be adequate to explain their experimental data on the quantum yields for the photochemical interconversion of the isomers. It is possible, however, that a further cause of the obliteration of fine structure in *cis*-stilbene is the lack of planarity in the ground state of the molecule (and probably in the excited state, although in the latter the equilibrium shape will differ from that of the ground state both in angles and in degree of non-planarity). Thus, for this reason also, practically every type of vibrational motion is expected to be excited in absorption, in contrast to the case of the *trans*-isomer with its more symmetrical, planar ground state and its planar or near-planar excited state. Both the loose-bolt effect and the non-planarity of the molecule might be expected to diminish at still lower temperatures, so that refrigeration far below −90° might remove these hindrances to the appearance of fine structure without differentiating between them. The non-planar ground state does not provide a ready explanation of lack of fluorescence in *cis*-stilbene. It is of interest that in the non-planar 2 : 4 : 6-trimethylstilbene (in 95% EtOH) fluorescence is reduced considerably below that of planar *trans*-stilbene.

In agreement with this emphasis on the vibrational consequences of the non-planar ground state, although not proving it, is the fact that *cis*-stilbene's A-band is shifted hypsochromically compared with *trans*-stilbene's. This probably results mainly from electronic differences due to non-coplanarity, however, and so far no theoretical treatment has predicted the amount of this shift.

## Experimental

At room temperatures, solutions of the compound in 95% or 100% ethanol or in hexane were examined in matched cells in the Beckman or Uvispek spectrophotometer. In each case cell corrections were applied to each optical-density reading to allow for any imbalance in absorption when both cells were filled with solvent. Readings were taken at 4 or 2 mμ intervals on slopes of the curves, the intervals being reduced to 1 or 0·5 mμ in the regions of maxima, minima, and shoulders. Reliance was placed only on optical density readings in the range 0·1—0·8, resulting in ε values with an estimated accuracy of ±0·5% for *trans*-stilbene in ethanol and ±1% for *cis*-stilbene and for *trans*-stilbene in hexane. *f*-Values were calculated as before (Beale and Roe, *loc. cit.*, 1952). Note that sublimation of the *trans*-stilbene specimen used before resulted in increases in ε values of <2% and in A-band *f*-value from 0·745 to 0·755.

Absorption measurements at low temperatures were made by a method already described (Beale and Roe, *J. Sci. Instr.*, 1951, **28**, 109), with the Hilger medium quartz spectrograph and Spekker photometer. Absorption by the mixed alcohol solvent in the 1·6-cm. cells required by this apparatus prevented accurate measurements below ~270 mμ. ε values were corrected for the changes in concentration resulting from contraction of solutions at −130° and are estimated to be accurate to ±3%.

The *trans*-stilbene used (m. p. 124°) was a commercial sample purified by repeated crystallisation from alcohol, followed by sublimation *in vacuo*. For the preparation of *cis*-stilbene the method of Taylor and Crawford (*J.*, 1934, 1140) was used, the oil being purified by repeated fractional distillation *in vacuo*; it had b. p. 134°/10 mm.

We are indebted to Professor C. Coulson, Dr. H. Greenwood, Professor M. Kasha, and Professor J. Platt for helpful discussion, to Mr. F. C. Middleton for assistance in the spectrophotometric measurements, and to Dr. G. Spickett for preparation of the *cis*-stilbene. This investigation has been supported by grants to the Royal Cancer Hospital and Chester Beatty Research Institute from the British Empire Cancer Campaign, the Jane Coffin Childs Memorial Fund for Medical Research, the Anna Fuller Fund, and the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service.

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## 555. *The Flavonoid Glycosides of* Dahlia variabilis. *Part I. General Introduction. Cyanidin, Apigenin, and Luteolin Glycosides from the Variety "Dandy."*

By C. G. Nordström and T. Swain.

The sap-soluble pigments responsible for flower colour in *Dahlia variabilis* are reviewed. A method for identification of flavones and their glycosides on a micro-scale is described. When applied to the compounds extracted from the flowers of the blue dahlia "Dandy" the presence of apigenin, its 4′- and 7-monoglucosides and 7-rhamnoglucoside, of luteolin 5-monoglucoside and 7-diglucoside, of cyanidin arabinoglucoside, and of a few minor compounds has been demonstrated.

*Introduction.*—The flower colour of garden varieties of *Dahlia variabilis* has been shown to depend on the presence of varying proportions of sap-soluble pigments of flavonoid type. Those which have been isolated from dahlia flowers are apigenin (Schmidt and Waschkau, *Monatsh.*, 1928, **49**, 83), luteolin, diosmetin (Nakaoki, *J. Pharm. Soc. Japan*, 1938, **58**, 639), butein (Price, *J.*, 1939, 1017), 2′ : 4 : 4′-trihydroxychalkone (Bate-Smith and Swain, *J.*, 1953, 2185), and cyanin (Willstätter and Mallinson, *Annalen*, 1915, **408**, 147). Robinson and Robinson (*Nature*, 1931, **128**, 413) showed the presence of pelargonin; and the 3-monoglucosides of pelargonidin and cyanidin were shown to be present in certain genotypes by Lawrence and Scott-Moncrieff (*J. Genetics*, 1935, **30**, 155). On the basis of their own and earlier chemical work the last authors related the genetic and the chemical evidence and showed that pigment distribution in the species falls into two colour groups: although anthocyanins and anthoxanthins could be present separately, the presence of the "yellow flavone" (afterwards shown to be butein and 2′ : 4 : 4′-trihydroxychalkone) in orange or scarlet flowers was accompanied specifically by a pelargonidin derivative, while the "ivory flavone" (apigenin and luteolin) in magenta, purple, and chocolate varieties was always associated with a cyanidin derivative. The "ivory flavone" was not present in yellow flowers. Schmidt and his co-workers (*loc. cit.*; *Monatsh.*, 1932, **60**, 32; 1933, **62**, 123) stated that both ivory and yellow pigments are non-glycosidic and, although Price (*loc. cit.*) indicated the possibility that butein glycosides may occur in yellow varieties, the only evidence that flavone glycosides are present in dahlia was the isolation of a diosmetin 7-rhamnoglucoside by Nakaoki (*loc. cit.*). Examination of a large number of garden varieties of dahlia (Bate-Smith, Swain, and Nordström, unpublished) by paper chromatography, while supporting in the main the conclusion reached by Lawrence and Scott-Moncrieff with regard to the anthoxanthin aglycones, showed that the anthoxanthins were present mainly as glycosides. The separation and identification of these compounds will be described in the present series of papers.

*Present Work.*—Although the complex mixture of phenolic glycosides present in many petal and other plant extracts may readily be separated by paper chromatography (Bate-Smith, *Biochem. Symp.*, 1949, No. 3, 62) the individual compounds cannot usually be identified by $R_F$ values and colour reactions alone (cf. Bradfield and Flood, *J.*, 1952, 4740) because there may be present a large number of glycosides related to a single aglycone (cf. Ice and Wender, *J. Amer. Chem. Soc.*, 1953, **75**, 50). Even direct measurement of ultraviolet absorption spectra on paper chromatograms (Bradfield and Flood, *loc. cit.*) does not permit differentiation between glycosides related to one aglycone (cf. Table 4). Attempts were made therefore to separate the mixture before examination of individual components. While this work was in progress Wender and his collaborators (references cited by Ice and Wender, *loc. cit.*) published a substantial contribution to the separation of flavonoid compounds present in various plant extracts, but, since they were concerned in the isolation of relatively large quantities of flavones for biological testing, the amount of original plant material used was very much greater than was available to us. Our preliminary experiments with partition columns gave poor results. We found, however, contrary to Gage and Wender (*Analyt. Chem.*, 1950, **22**, 708) and Bradfield and Flood (*loc. cit.*), that provided

the solvent is removed from developed paper chromatograms at room temperature, individual bands can be quantitatively eluted in 24—48 hr. with aqueous alcohol. The extracted bands may be then further purified if necessary by use of a second solvent. [When this work was completed Linstedt and Misiorny (*Svensk Papperstidning*, 1952, **55**, 602) and Williams and Wender (*J. Amer. Chem. Soc.*, 1952, **74**, 5919) described similar techniques for eluting flavonoid compounds although the elution time (2 hr.) used by the latter authors was possibly too short for complete extraction.] In this way it was possible in some cases to isolate sufficient material for both melting-point determination and analysis; but the nature of the compounds obtained has been established mainly by the methods indicated by Nordström *et al.* (*Chem. and Ind.*, 1953, 85) for identification of material in microgram quantities. Normally there are not more than two phenolic aglycones of any one type (*e.g.*, flavones, chalkones, etc.) represented as glycosides in the extracts from single plant varieties. These, whether occurring free or obtained from the glycosides on hydrolysis, can be identified with certainty by comparing their spectra in ethyl alcohol and 0·002M-sodium ethoxide (Mansfield, Swain, and Nordström, *Nature*, 1953, **172**, 23), $R_F$ values in various solvents (Bate-Smith and Westall, *Biochim. Biophys. Acta*, 1950, **4**, 427; Gage, Douglass, and Wender, *Analyt. Chem.*, 1951, **23**, 1582) or on borate-impregnated filter paper (Wachmeister, *Acta Chem. Scand.*, 1951, **5**, 976; cf. Bate-Smith and Swain, *loc. cit.*), and their colour reactions (especially fluorescence) with synthetic standards. The sugars occurring in phenolic glycosides can be readily identified, after hydrolysis and removal of acid with a basic ion-exchange resin (cf. Piez, Tooper, and Fosdick, *J. Biol. Chem.*, 1952, **194**, 669), by $R_F$ values and colour reactions (Partridge, *Biochem. J.*, 1948, **42**, 238; cf. Ice and Wender, *loc. cit.*).

The number of sugar groups attached to each aglycone in the purified glycosides can be tentatively deduced from the $R_M$ value * (Bate-Smith and Westall, *loc. cit.*), but it can be determined more accurately after careful hydrolysis of each component (*ca.* 0·2 mg.) by estimation of the resulting aglycone spectrophotometrically and the sugar either by Somogyi's copper micro-method (*J. Biol. Chem.*, 1952, **195**, 19), or by the anthrone reagent (Morris, *Science*, 1948, **107**, 254), hydrolysis being unnecessary in the latter case. The anthrone method is especially useful for glycosides containing rhamnose since low concentrations of this sugar give erratic results with the Somogyi reagent. For diglycosides where the two sugars are different the concentration of each may be determined by either of the above methods after separation and elution from paper chromatograms. When our work was complete Ice and Wender (*loc. cit.*) described the determination of the sugar concentration in the hydrolysates of a quercetin diglucoside by the method of Fisher, Parsons, and Morrison (*Nature*, 1948, **161**, 764) but we had abandoned this technique since it gave unreliable results with our material.

The position of the carbohydrate moiety in the separated glycosides has been determined by methylation followed by hydrolysis, the partially methylated aglycone being identified by methods similar to those described above for the free flavones. In this connection spectra of the compounds in 0·002M-sodium ethoxide have been of great diagnostic value (Mansfield *et al.*, *loc. cit.*).

The spectral shifts and changes in intensity in bands I and II for 3′ : 4′ : 5- and 3′ : 5 : 7-tri-*O*-methyl-luteolin (Figure) are similar to those found for the corresponding apigenin derivatives. The corresponding 3′ : 4′ : 7-tri-*O*-methyl-luteolin behaves similarly.

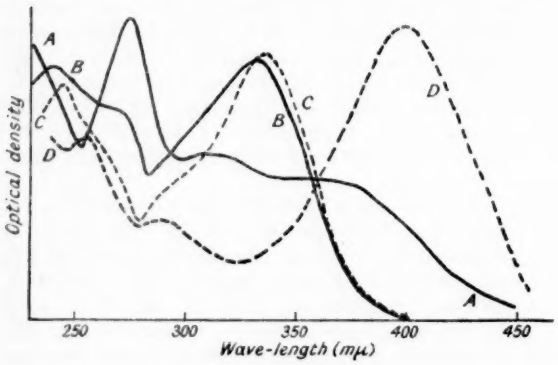
The order of monosaccharides in the case of biosides containing two different sugars was determined by separation and examination of the intermediate monoside resulting from partial hydrolysis (cf. Nordström *et al.*, *loc. cit.*). Application of all these methods of identification permits determination of the nature of the separated glycosides with only 1 mg. of each.

The ethanolic hydrochloric acid extracts of the petals of the purple-blue garden dahlia "Dandy," when examined in this way, showed the presence of six components after separation on pre-washed paper by butanol–acetic acid–water. Three of the components could be further separated in either butanol–water or *iso*propanol–2N-hydrochloric acid

* $R_M = \log [(1/R_F) - 1]$. It varies directly with the number of functional groups.

(Table 1). The ethyl acetate-soluble portion of the hydrolysed extract was separated into two flavones. The flavone present in larger amount had the same colour reactions and $R_F$ values (Table 2) as apigenin (I; R = R′ = H), and was isolated on a larger scale by paper chromatography and identified by analysis and its mixed melting point. The flavone present in minor amount was not isolated in sufficient quantity for a melting-point determination but from its $R_F$ values and colour reactions (Table 2) was identified as luteolin (II; R = R′ = H). The presence of both compounds in one variety of dahlia had been shown previously by Nakaoki (*loc. cit.*), but unlike the Japanese worker we have not yet found even a trace of diosmetin or its derivatives in any dahlia we have examined.

Thus the main flavonoid components in the unhydrolysed extract (Table 1) were expected to be related to apigenin and luteolin, and this has been borne out by the results. Band I was shown to be apigenin itself (Tables 2 and 4), which was isolated on a larger scale and identified. Its concentration is higher in the extract examined than in extracts from fresh petals, presumably owing to hydrolysis during storage (6 months at 0°).




*A*, 3′ : 4′ : 5-*Tri*-O-*methyl-luteolin in* 0·002M-*sodium ethoxide.*
*B*, 3′ : 4′ : 5-*Tri*-O-*methyl-luteolin in ethanol.*
*C*, 3′ : 5 : 7-*Tri*-O-*methyl-luteolin in ethanol.*
*D*, 3′ : 5 : 7-*Tri*-O-*methyl-luteolin in* 0·002M-*sodium ethoxide.*

Band 2 was shown to be a glycoside since on treatment with acid it showed the presence of luteolin (Tables 2 and 4) and glucose (Table 3), and its $R_F$ value in ethyl acetate–water was low (Table 2) (cf. Swain, *Biochem. J.*, 1953, **53**, 200). From its $R_M$ value it was obviously a monoside and this was proved by quantitative analysis (Table 5). On

TABLE 1. *Separation, identification, and relative concentration of the flavonoid glycosides.*

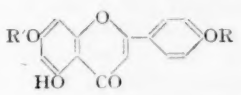
| Band no. | $R_F$ in: BuOH–AcOH–$H_2O$ (6 : 1 : 2) | BuOH–$H_2O$ | PrⁱOH–2N-HCl (1 : 1) | Identified as | Relative concn. |
|---|---|---|---|---|---|
| 1 | 0·89 | 0·88 | — | Apigenin | 26 |
| 2 | 0·75 | 0·60 | — | Luteolin 5-glucoside | 8 |
| 3·1 | 0·62 | 0·59 | — | Apigenin 4′- and 7-glucoside | 40 |
| 3·2 | | 0·12 | — | Apigenin 4′- and 7-glucoside & naringenin glucoside | 12 |
| 4 | 0·49 | 0·27 | — | Apigenin 7-rhamnoglucoside | 100 [a] |
| 5·1 | 0·23 | 0·09 | — | Unknown diglucoside | — |
| 5·2 | | 0·05 | | Luteolin 7-diglucoside | 27 |
| 6·1 | 0·18 | — | 0·34 | Pelargonidin glycoside | — |
| 6·2 | | | 0·24 | Cyanidin 3 : 5(?)-arabinoglucoside | 8 [b] |

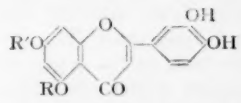
[a] Actual concn. 1·3 mg. per ml. of extract. [b] As cyanin.

methylation with methyl sulphate and potassium carbonate in acetone and subsequent hydrolysis a compound was obtained which, since it gave a negative reaction with ferric chloride, was presumably tetra-*O*-methyl-luteolin, and it was obvious that hydrolysis of the glucoside followed by methylation of the free hydroxyl group had occurred. Since glycosides in which the sugar is attached to the 4′- or the 7-hydroxyl group in flavones are not affected under these conditions (see below) it appeared probable that band 2 was due

to a 5-glucoside. This was proved by methylation with diazomethane to a product giving a negative ferric chloride reaction (unlike the luteolin 7-diglucoside, band 5·2, see below). On hydrolysis with acid, the sugar-free methyl ether gave a dark brown colour with ferric chloride, thus showing the presence of a free 5-hydroxyl group. The spectrum of the product was similar to those of 3′ : 4′ : 7-tri-*O*-methyl-luteolin, but examination on a paper chromatogram showed that tetra-*O*-methyl-luteolin was also present (Tables 6 and 7). However the spectrum of band 2 itself in sodium ethoxide solution (Table 4) indicates the presence of both a free 7- and a free 4′-hydroxyl group (cf. 3′ : 4′ : 5- and 3′ : 5 : 7-tri-*O*-methyl-luteolin, Table 7) and taken in conjunction with the positive ferric reaction shows that this band is due to luteolin 5-glucoside (II; R = glucosyl; R′ = H).

Luteolin 5-glucoside (galuteolin) has been isolated previously from *Galega officinalis* (Barger and White, *Biochem. J.*, 1923, **17**, 836) and *Equisetum arvense* (Nakamura and Hukuti, *J. Pharm. Soc. Japan*, 1940, **60**, 449).

(I) 

(II)

Band 3 was due to a mixture, which gave components 3·1 and 3·2 by separation in butanol–water (Table 1). The faster-running component (3·1) gave apigenin and glucose only on hydrolysis (Tables 2 and 3), and quantitative examination showed it to be an apigenin monoglucoside (Table 5). On methylation and hydrolysis however it gave a product which was separable in butanol–water on borate- or phosphate-impregnated filter paper into two aglycones having $R_F$ values and colour reactions identical with those of 4′ : 5- and 5 : 7-di-*O*-methylapigenin (Table 6). The easy separation of these two ethers on alkaline-buffered paper is presumably due to a difference in acidity, the 4′ : 5-di-*O*-methyl ether being, as expected, the more acidic (Table 6). Similar differences in acidity of 4′- and 7-hydroxy-groups have been disclosed by partial methylation of 4′ : 7-dihydroxyflavone (Beton and Simpson, unpublished results; cf. Narasimhachari and Seshadri, *Proc. Indian Acad. Sci.*, 1950, **32**, *A*, 256). The spectra of the methylated product in 0·002M-sodium ethoxide (Table 7) also indicated the presence of these two compounds. Thus, although the original monoglucoside component (3·1) could not be separated in any solvent system tried, it is obviously a mixture of apigenin 7- (I; R = H, R′ = glucosyl) and 4′-glucoside (I; R = glucosyl, R′ = H). Apigenin 7-glucoside (cosmetin) has been isolated from *Cosmos bipinatus* (Nakaoki, *J. Pham. Soc. Japan*, 1935, **55**, 173); when obtained by partial hydrolysis of apiin (cf. Nordström *et al.*, *loc. cit.*) it had the same $R_F$ values (Table 2) as the mixture (3·1) in all solvents tried. Apigenin 4′-glucoside has not been reported previously; indeed except for the two genistein 4′-glycosides isolated from *Sophora japonica* (Bognàr, *Magyar Kem. hapja*, 1949, **4**, 519; *Chem. Abs.*, 1952, **46**, 8104) no other flavonoid 4′-glycoside has been reported.

The second component causing band 3 (3·2) was also a mixture, since it yielded apigenin and small quantities of naringenin (Table 2), together with glucose (Table 3), on hydrolysis. The spectra of the mixture of aglycones (Table 4) produced also indicated the presence of both compounds. Methylation and subsequent hydrolysis of 3·2 yielded a product, the $R_F$ values and colour reactions of which indicated the presence of both 4′ : 5- and 5 : 7-di-*O*-methylapigenin (Table 6). The $\lambda_{max.}$ in the spectra of the product confirmed this although owing to the low concentration and presence of impurities the relative intensities could not be determined accurately. The apigenin monoglucosides present in band (3·2) therefore are the same as those in band (3·1) and the separation of these bands may be due to the formation of a molecular complex between the apigenin components of (3·2) and the naringenin derivative present. Attempts to separate further either band (3·1) or (3·2) met with no success.

Band 4, as can be seen from Table 1, is the major compound in the extract. It was shown to be a rhamnoglucoside of apigenin (Tables 2, 3, and 4) and quantitative examination gave an apigenin–sugar ratio of 1 : 2·2 (Table 5). Methylation followed by hydrolysis

gave a product identical with 4' : 5-di-*O*-methylapigenin (Tables 6 and 7). On partial hydrolysis apigenin 7-glucoside was obtained (Tables 2 and 3), and band 4 is therefore apigenin 7-rhamnosylglucoside (I; R = H, R' = rhamnosylglucosyl). A compound of this structure has been isolated from *Rhus succedanea* (Hattori and Matsuda, *Arch. Biochim. Biophys.*, 1952, **37**, 85) and assumed to be a rutinoside. Sufficient material was isolated from band 4 for melting-point determination, recrystallisation and analysis, and was identical with rhoifolin kindly supplied by Professor Hattori. The $R_F$ values, colour reactions, and spectra of rhoifolin were the same as for band 4 (Tables 2 and 4).

Band 5 was shown to contain two components separable in butanol–water. The major component (5·2) was a luteolin diglucoside (Tables 2—5), and methylation followed by hydrolysis showed that the sugar was attached to the 7-position. Since it was found that band 2 (luteolin 5-glucoside) was hydrolysed during methylation with methyl sulphate, the position of the sugar in the diglucoside (5·2) was confirmed by methylation with diazomethane. In this case the product obtained gave a brown colour with ferric chloride solution before hydrolysis, showing that the 5-hydroxyl group was free. Band 5·2 is therefore luteolin 7-diglucoside (II; R = H, R' = glucosylglucosyl). No compound of this structure has been so far reported in Nature. The second component (5·1) gave glucose and a mixture of two aglycones on hydrolysis, neither of which has been so far identified. Band (5·1) was in too low a concentration for further work to be carried out but from its position it was presumably a mixture of diglucosides.

The anthocyanin band (6) was separated into two compounds with *iso*propanol–2N-hydrochloric acid (Table 1). The major component on hydrolysis gave cyanidin (identified by its $R_F$ value in butanol–2N-hydrochloric acid and distribution tests), arabinose, and glucose (Table 3). It is probably a 3 : 5-diglycoside but owing to fading of the aglycone at low concentrations a quantitative determination was not possible. An arabinoglucoside of cyanidin has been reported in the beans of *Forastero cacao* (Forsyth, *Biochem. J.*, 1952, **51**, 511). The second anthocyanin was present in too low concentration for complete identification, but on hydrolysis gave an aglycone indistinguishable from pelargonidin.

The reference compounds required for this investigation were prepared by oxidative cyclisation from the corresponding chalkones.

## Experimental

M. p.s are corrected.

*Separation of the Flavonoid Compounds from " Dandy ".*—Petals (88·5 g.) of " Dandy " (a blue garden variety of *Dahlia variabilis*) were crushed under 0·01N-ethanolic hydrochloric acid (400 ml.), kept at 0° for 1 week, and filtered (total solids, 14·5 mg./ml.; total sugar, 6 mg./ml.). The extract (10 ml.) was applied as a streak from a teat pipette in 0·5—1-ml. portions to Whatman's No. 3 paper 22 × 18", which had been previously washed with water for 24 hr. in a chromatographic cabinet and dried at room temperature. The chromatogram was developed overnight with butanol–acetic acid–water (6 : 1 : 2) (this approximates to the organic phase of the conventional 4 : 1 : 5 solvent) and carefully dried in a current of air in a fume cupboard. The positions of the bands were marked under an ultra-violet lamp. The separated components were eluted from the paper in a conventional chromatographic tank with either cold aqueous ethanol (40—70%, more aqueous solvents being used for components having low $R_F$ values) for the flavones, or cold aqueous dilute hydrochloric acid for the anthocyanins. This process took 1—3 days. Each of the resulting solutions was concentrated to small volume *in vacuo* and purified by re-running in the same solvent system and elution as before. The purified bands were then tested for homogeneity on Whatman's No. 1 paper in other solvents and, when mixtures, separated in a similar way to that used for the original extract. Compounds having $R_F$ values less than 0·4 in butanol–acetic acid–water (6 : 1 : 2), except the anthocyanins, were separated from free sugars on Whatman's No. 3 paper by acetone–water (1 : 3) in which the flavones have much lower $R_F$ values (0—0·1) than those of the sugars (0·8—0·9). The anthocyanin band was freed from the faster-running sugars ($R_F$ 0·7—0·8) during separation by *iso*propanol–2N-hydrochloric acid. The results of the primary separation are given in Table 1.

*Examination of the Separated Flavone Glycosides.*—The $R_F$ values in several solvents and

TABLE 2. *$R_F$ values and colour reactions of the glycosides and corresponding aglycones.*

| Compound [a] | $R_F$ in: BuOH–AcOH–$H_2O$ (6 : 1 : 2) | BuOH–$H_2O$ Plain paper | BuOH–$H_2O$ Borate paper [b] | BuOH–$H_2O$ Phosphate paper [c] | EtOAc–$H_2O$ Plain paper | EtOAc–$H_2O$ Borate paper [b] | EtOAc–$H_2O$ Phosphate paper [c] | $COMe_2$–$H_2O$ (1 : 1) | Colour reactions: u.-v. light | Colour reactions: u.-v. light + $NH_3$ vapour |
|---|---|---|---|---|---|---|---|---|---|---|
| Aglycone 1 from hydrolysed extract | 0·89 | 0·88 | 0·46 | 0·84 | 0·88 | — | — | 0·59 | Dark ochre | Bright green |
| Aglycone 2 from hydrolysed extract | 0·82 | 0·73 | 0·02 | 0·69 | 0·86 | — | — | 0·31 | ,, | Green-yellow |
| Band 1 | 0·89 | 0·88 | 0·46 | 0·84 | 0·88 | 0·75 | 0·87 | 0·59 | ,, | Bright green |
| ,, 2 | 0·75 | 0·60 | 0·02 | 0·26 | 0 | — | — | 0·42 | ,, | Green-yellow |
| ,, 3·1 | 0·62 | 0·42 | 0·15 | 0·32 | 0·12 | — | — | 0·59 | ,, | Bright green |
| ,, 3·2 | 0·62 | 0·19 | 0·04 | 0·04 | 0·12 | — | — | 0·59 | ,, | ,, |
| ,, 4 | 0·40 | 0·27 | 0·04 | 0·17 | 0·01 | — | — | 0·69 | ,, | ,, |
| ,, 5·1 | 0·23 | 0·09 | 0·06 | 0·07 | 0 | — | — | 0·53 | Light ochre | ,, |
| ,, 5·2 | 0·23 | 0·05 | 0·02 | 0·04 | 0 | — | — | 0·38 | Dark ochre | Green-yellow |
| Partially hydrolysed band 4 | 0·59 | 0·42 | — | — | — | — | — | 0·49 | ,, | Bright green |
| Partially hydrolysed band 5·2 | 0·39 | 0·21 | — | — | — | — | — | 0·45 | ,, | Green-yellow |
| Aglycone from band 2 | 0·82 | 0·73 | 0·02 | 0·69 | 0·86 | 0 | 0·80 | 0·31 | ,, | ,, |
| ,, ,, 3·1 | 0·89 | 0·86 | 0·46 | 0·84 | 0·91 | 0·75 | 0·87 | 0·59 | ,, | Bright green |
| ,, ,, 3·2 | 0·89 | 0·89 | 0·46 | 0·84 | 0·91 | 0·75 | 0·87 | 0·59 | ,, | ,, |
| ,, ,, 3·2 | 0·95 | 0·89 | 0·88 | — | — | — | — | 0·79 | Light ochre | Green |
| ,, ,, 4 | 0·89 | 0·87 | 0·46 | 0·84 | 0·90 | 0·75 | 0·87 | 0·61 | Dark ochre | Bright green |
| ,, ,, 5·1 | 0·92 | 0·91 | 0·94 | 0·87 | 0·92 | 0·96 | 0·90 | 0·71 | Green | Green |
| ,, ,, 5·1 | 0·79 | 0·74 | 0·44 | — | — | — | — | 0·89 | Light green | ,, |
| ,, ,, 5·2 | 0·82 | 0·73 | 0·02 | 0·69 | 0·86 | 0 | 0·80 | 0·59 | Dark ochre | Green-yellow |
| Rhoifolin | 0·40 | 0·23 | 0·04 | 0·17 | — | — | — | 0·64 | ,, | Bright green |
| Apigenin 7-glucoside [d] | 0·59 | 0·42 | 0·15 | 0·32 | — | — | — | 0·49 | ,, | ,, |
| Luteolin 7-glucoside [d] | 0·39 | 0·21 | — | — | — | — | — | 0·42 | ,, | Green-yellow |
| Apigenin | 0·89 | 0·88 | 0·46 | 0·84 | 0·90 | 0·75 | 0·87 | 0·59 | ,, | Bright green |
| Luteolin | 0·82 | 0·73 | 0·02 | 0·69 | 0·86 | 0 | 0·80 | 0·31 | ,, | Green-yellow |
| Naringenin | 0·93 | 0·89 | 0·88 | 0·87 | 0·93 | 0·91 | 0·91 | 0·79 | Light ochre | Green |

[a] See Table 1. [b] $R_F$ dependent to some extent on amount of material applied. [c] Papers must be run as soon as possible after preparation. [d] Prepared from partially hydrolysed "crude apiin" (Nordström *et al., loc. cit.*).

colour reactions of the glycosides were determined on Whatman's No. 1 paper. The results are given in Table 2.

The ultra-violet absorption spectra of the glycosides in ethyl alcohol and 0·002M-sodium ethoxide solution were determined as described by Mansfield *et al.* (*loc. cit.*). The reference solvent was prepared separately for each glycoside by eluting a strip of the same $R_F$ value from a blank chromatogram and treating it as in the purification of the glycoside itself. The results are shown in Table 4.

*Identification of the Flavone Glycosides.*—(a) *Qualitative hydrolysis.* The glycoside (*ca.* 100 μg.) in alcohol (1 ml.) and 2N-sulphuric acid (1 ml.) was heated at 100° for 1 hr., then cooled,

TABLE 3. *Identification of the sugars produced by hydrolysis of " Dandy " glycosides.*

| Sugar from band [a] | $R_F$ values in: BuOH–AcOH–$H_2O$ (6 : 1 : 2) | PhOH–$H_2O$ | EtOAc–pyridine–$H_2O$ [b] (2 : 1 : 2) | Colour with *p*-anisidine hydrochloride [c] |
|---|---|---|---|---|
| 2 | 0·15 | 0·38 | 0·28 | Brown |
| 3·1 | 0·15 | 0·38 | 0·31 | Brown |
| 3·2 | 0·15 | 0·38 | 0·31 | Brown |
| 4 | 0·15 | 0·38 | 0·28 | Brown |
| | 0·34 | 0·64 | 0·54 | Light brown |
| 5·1 | 0·15 | 0·37 | 0·28 | Brown |
| 5·2 | 0·15 | 0·37 | 0·28 | Brown |
| 6·2 | 0·15 | 0·38 | 0·28 | Brown |
| | 0·19 | 0·54 | 0·32 | Red |
| Partially hydrolysed band 4 | 0·15 | 0·38 | 0·28 | Brown |
| Glucose | 0·15 | 0·38 | 0·28 | Light brown |
| Rhamnose | 0·34 | 0·64 | 0·54 | Brown |
| Arabinose | 0·19 | 0·54 | 0·32 | Red |

[a] See Table 1. [b] Jermyn and Isherwood, *Biochem. J.*, 1949, **44**, 402. [c] Hough, Jones, and Wadman, *J.*, 1950, 1702.

TABLE 4. $\lambda_{max.}$, $\Delta\lambda$, and $\Delta D(\%)$ *of the ultra-violet absorption spectra in ethyl alcohol and* 0·002M-*sodium ethoxide of the glycosides and corresponding aglycones.*

| Compound [a] | Band I $\lambda_{max.}$ (EtOH) | Band I $\Delta\lambda$ [b] | Band I $\Delta D$ (%) [c] | Band II $\lambda_{max.}$ (EtOH) | Band II $\Delta\lambda$ [b] | Band II $\Delta D$ (%) [c] |
|---|---|---|---|---|---|---|
| Band 1 | 335 | 63 | 44 | 269 | 10 | 17 |
| ,, 2 | 349 | 51 | −26 | 265 | 5 | 45 |
| ,, 3·1 | 334 | 57 | 18 | 270 | 5 | 24 |
| ,, 3·2 | 340 | 56 | 1 | 270 | 6 | 6 |
| ,, 4 | 335 | 63 | 98 | 268 | 0 | −21 |
| ,, 5·1 | 335 | 65 | 43 | 268 | 4 | 24 |
| ,, 5·2 | 350 | 52 | 12 | 259 | 8 | 18 |
| Aglycone from band 2 | 350 | 54 | 19 | 258 | 12 | 29 |
| ,, ,, 3·1 | 335 | 63 | 51 | 270 | 7 | 29 |
| ,, ,, 3·2 | 335 | 63 | 43 | 270 | 7 | 17 |
| ,, ,, 3·2 | — | — | — | 290 | 40 | 12 |
| ,, ,, 4 | 335 | 64 | 83 | 269 | 10 | 18 |
| ,, ,, 5·1 | 325 | 65 | −32 | 275 | 55 | − 1 |
| ,, ,, 5·2 | 350 | 54 | 34 | 258 | 10 | 20 |
| Rhoifolin | 335 | 60 | 72 | 270 | 0 | − 6 |
| Apigenin 7-glucoside | 335 | 63 | 66 | 268 | 1 | −20 |
| Apigenin | 335 | 63 | 67 | 269 | 10 | 32 |
| Luteolin | 351 | 52 | 39 | 256 | 13 | 14 |
| Naringenin | — | — | — | 286 | 43 | 35 |

[a] See Table 1. [b] $\Delta\lambda$ is the difference in $\lambda_{max.}$ of the band in ethyl alcohol and 0·002M-sodium ethoxide. [c] $\Delta D$ (%) is the difference (%) in the optical density at the peak in alcohol and 0·002M-sodium ethoxide.

and the aglycone was extracted with ethyl acetate. The extract was washed with water and after removal of the solvent the flavone dissolved in alcohol (*ca.* 0·5 ml.). Each aglycone was identified by comparing its $R_F$ values in various solvents, colour reactions, and ultra-violet absorption spectra with synthetic standards. The reference solvent for the spectra of the

aglycones was prepared by treating the solutions used for the glycosides under the same conditions of hydrolysis. The results are shown in Tables 2 and 4.

The aqueous phase and the washings from the hydrolysis were combined, and the acid was removed with the bicarbonate form of the basic ion-exchange resin "Dowex 2" (prepared according to Piez *et al.*, *loc. cit.*). The resin was removed by centrifuging and washed with water, and the aqueous liquors were concentrated to *ca.* 0·5 ml. for identification of the sugars. The results are shown in Table 3.

(b) *Quantitative hydrolysis.* (i) Determination of aglycone concentration. The glycoside (*ca.* 100—300 μg.) in alcohol (2 ml.) and 2N-sulphuric acid (2 ml.) was heated for 2 hr. at 100° under reflux, cooled, and diluted to a known volume (depending on concentration) with alcohol. The concentration of the aglycone was determined spectrophotometrically, standards being previously determined in the same acid medium.

(ii) Determination of sugar concentration. A second portion of the glycoside solution used for the above determination (volume depending on sugar concentration) was taken to dryness in a ¾" standard colorimeter tube (Unicam D.G. spectrophotometer), and anthrone solution (10 ml.; 0·2% in 95% sulphuric acid) followed by water (5 ml.) added. The contents were mixed and the absorbance measured at 620 mμ after 15 min. A control experiment with the corresponding sugar was carried out simultaneously, the sugar solution being in this case added directly to the reagent. This method of addition (water or sugar solution to reagent) gave more reproducible results than the conventional reverse procedure (Morris, *loc. cit.*). The results are shown in Table 5.

TABLE 5. *Aglycone : sugar ratio for the glycosides.*

| | Concn. (mg./ml.) | | | | Concn. (mg./ml.) | | |
|---|---|---|---|---|---|---|---|
| Band [a] | Aglycone [b] | Glucose | Aglycone : sugar [b] | Band [a] | Aglycone [b] | Glucose | Aglycone : sugar [b] |
| 2 | 0·080 | 0·058 | 1 : 1·14 | 4 | 0·455 | 0·334 [d] | 1 : 1·10 : 1·10 |
| | 0·095 | 0·066 | 1 : 1·12 | | 0·455 | 0·340 [e] | 1 : 1·12 : 1·12 |
| 3·1 | 0·340 | 0·268 | 1 : 1·18 | 5·2 | 0·140 | 0·198 | 1 : 2·24 |
| | 0·360 | 0·276 | 1 : 1·14 | | 0·130 | 0·182 | 1 : 2·22 |
| 3·2 | 0·077 A, 0·022 N | 0·063 | 1 : 0·96 A [c] | | | | |
| | 0·106 A, 0·013 N | 0·077 | 1 : 0·98 A [c] | | | | |

[a] See Table 1. [b] A = Apigenin; N = naringenin. [c] Based on naringenin : glucose = 1 : 1. [d] Also rhamnose 0·306 mg./ml. [e] Also rhamnose 0·310 mg./ml.

*Determination of the Position of Sugar Substituent.*—(*a*) The glycoside (*ca.* 500 μg.), anhydrous potassium carbonate (0·1 g.), and freshly distilled methyl sulphate (0·1 ml.) were refluxed for 6 hr. in dry acetone (2 ml.). The solvent was removed under reduced pressure and the product heated with 2N-sulphuric acid (3 ml.) for 2 hr. at 100°. On cooling, the partially methylated aglycone was extracted with chloroform, the extract washed with water, and after removal of the solvent the compound was dissolved in alcohol. The partial methyl ethers were then identified by comparing their $R_F$ values, colour reactions, and ultra-violet absorption spectra with those of synthetic standards. As in the previous case, the reference solutions were prepared by treating the eluates from the blank chromatograms as described above. The results are shown in Tables 6 and 7.

(*b*) Methylation of bands 2 and 5·2 with diazomethane was carried out in the normal manner.

*Identification of the Anthocyanidin Glycosides.*—Qualitative hydrolysis of the main anthocyanidin component (band 6·2, Table 1) was carried out in a manner similar to that described for the flavones. The aglycone was extracted with amyl alcohol. By distribution tests (Robinson and Robinson, *Biochem. J.*, 1931, **25**, 1693) and its $R_F$ value (0·70 in butanol–2N-hydrochloric acid; Bate-Smith, *loc. cit.*), it was shown to be cyanidin ($R_F$ 0·70). The aqueous solution, after removal of acid, showed the presence of arabinose and glucose (Table 3).

Attempts to estimate the cyanidin resulting from hydrolysis were abandoned since the colour faded at the concentration used. It was not possible therefore to determine the sugar : aglycone ratio.

The second anthocyanin band (6·1; Table 1) on hydrolysis and extraction with amyl alcohol as above gave an aglycone having the same $R_F$ value (0·81 in butanol–2N-hydrochloric acid) and colour reactions as pelargonidin. The sugars were in too low concentration to be identified.

*Isolation of Apigenin from "Dandy."*—(*a*) The original extract (100 ml.) was heated with an equal volume of 2N-hydrochloric acid for 2 hr. at 100°. The cooled solution was extracted

with ethyl acetate (3 × 200 ml.), and the extract washed with water, taken to small volume, and separated on Whatman's No. 3 paper in butanol–acetic acid–water (6 : 1 : 2) as described above. The major component ($R_F$ 0·89) was eluted with 70% alcohol, and most of the alcohol

TABLE 6. *$R_F$ values and colour reactions of the partial methyl ethers obtained from the glycosides.*

| | $R_F$ in : | | | Colour | |
|---|---|---|---|---|---|
| Partial methyl ether from band [a] | $C_6H_6$–$MeNO_2$–$H_2O$ [b] (3 : 2 : 5) | BuOH–$H_2O$ Borate paper | BuOH–$H_2O$ Phosphate paper | u.-v. light | u.-v. light + $NH_3$ vapour |
| 2 [c] | 0·95 (0·91) | 0·92 (0·80) | 0·77 (0·55) | Brown (blue) | Brown (blue) |
| 3·1 | 0·46 | 0·80 | 0·70 | Blue | Green-blue |
| | 0·46 | 0·51 | 0·62 | V. pale blue | Yellow |
| 3·2 | 0·46 | 0·80 | 0·70 | Blue | Green-blue |
| | 0·46 | 0·51 | 0·62 | V. pale blue | Yellow |
| 4 | 0·46 | 0·51 | 0·62 | V. pale blue | Yellow |
| 5·2 | 0·35 | 0·26 | 0·34 | Pale lilac | Orange-yellow |
| 4′ : 5-Di-*O*-methylapigenin ..... | 0·46 | 0·51 | 0·62 | V. pale blue | Yellow |
| 4′ : 7- ,, [c] ..... | 0·97 | 0·93 | 0·84 | Brown | Brown |
| 5 : 7- ,, ..... | 0·46 | 0·80 | 0·70 | Blue | Green-blue |
| Tri-*O*-methylapigenin ..... | 0·91 | 0·87 | 0·79 | Blue | Blue |
| 3′ : 4′ : 5-Tri-*O*-methyl-luteolin | 0·35 | 0·26 | 0·34 | Pale lilac | Orange-yellow |
| 3′ : 4′ : 7- ,, [c] ..... | 0·95 | 0·92 | 0·77 | Brown | Brown |
| 3′ : 5 : 7- ,, ..... | 0·72 | 0·67 | 0·55 | V. pale blue | Yellow-green |
| 4′ : 5 : 7- ,, ..... | 0·73 | 0·77 | 0·55 | Dark blue | Red-purple |
| Tetra-*O*-methyl-luteolin ..... | 0·91 | 0·80 | 0·55 | Blue | Blue |

[a] See Table 1. [b] Simpson and Garden, *J.*, 1952, 4638. [c] Gave a positive ferric chloride reaction.

TABLE 7. *$\lambda_{max.}$, $\Delta\lambda$, and $\Delta D(\%)$ of the ultra-violet absorption spectra in ethyl alcohol and 0·002M-sodium ethoxide of the partial methyl ethers from the glycosides.*

| | Band I | | | Band II | | |
|---|---|---|---|---|---|---|
| Partial methyl ether from band [a] | $\lambda_{max.}$ (EtOH) | $\Delta\lambda$ [b] | $\Delta D$ (%) [c] | $\lambda_{max.}$ (EtOH) | $\Delta\lambda$ [b] | $\Delta D$ (%) [c] |
| 2 | 335 | — | — | 270 | 18 | 1 |
| 3·1 | 327 | 53 | 5 | 262 | 7 | 29 |
| 3·2 | 325 | 50 | 4 | 260 | 8 | 40 |
| 4 | 325 | 38 | −32 | 264 | 10 | 63 |
| 5·2 | 334 | 26 | −43 | 242 | 33 | 15 |
| 4′ : 5-Di-*O*-methylapigenin ..... | 325 | 35 | −32 | 260 | 12 | 70 |
| 4′ : 7- ,, ..... | 325 | — | — | 271 | 21 | 28 |
| 5 : 7- ,, ..... | 327 | 53 | 48 | 259 | 3 | −10 |
| Tri-*O*-methylapigenin ..... | 322 | 0 | 0 | 265 | 0 | 0 |
| 3′ : 4′ : 5-Tri-*O*-methyl-luteolin | 333 | 27 | −35 | 240 | 35 | 46 |
| 3′ : 4′ : 7- ,, | 338 | — | — | 272 | 16 | 1 |
| 3′ : 5 : 7- ,, | 335 | 65 | 35 | 245 | 10 | −4 |
| 4′ : 5 : 7- ,, | 334 | 46 | −48 | 245 | 14 | 37 |
| Tetra-*O*-methyl-luteolin ..... | 330 | 0 | 0 | 240 | 0 | 0 |

[a] See Table 1. [b, c] As for Table 4.

removed, yielding a dark brown solid. Recrystallisation of this from aqueous alcohol gave pale yellow crystals (27·5 mg.), m. p. 340°, which did not depress the melting point of synthetic apigenin (Found : C, 65·9, 66·4; H, 5·9, 6·2. Calc. for $C_{15}H_{10}O_5$ : C, 66·7; H, 3·7%). The $R_F$ values and colour reactions of the product from " Dandy " were identical to those of synthetic apigenin (Table 2).

(*b*) Removal of the alcohol from the eluate of band 1 (Table 1) from 40 ml. of original extract gave a precipitate which after recrystallisation from aqueous alcohol gave pale yellow crystals (2·4 mg.), m. p. 340° alone or admixed with synthetic apigenin.

*Isolation of Rhoifolin from " Dandy ".*—The material is band 4 (Table 1) from 30 ml. of original extract was purified as described above, yielding a brown amorphous solid, m. p. 263—265° (decomp.; softens at 200—205°) alone or mixed with rhoifolin supplied by Professor Hattori (Found : C, 51·9, 51·6; H, 5·7, 5·7. Calc. for $C_{27}H_{30}O_{14}.3H_2O$ : C, 51·3; H, 5·7%)

(Hattori and Matsuda, *loc. cit.*, state that rhoifolin forms a trihydrate which softens at 200—203° and melts at 265° with decomp.).

*Partial Hydrolysis Material of Bands* 4 *and* 5·2 *from "Dandy."*—The glycoside (*ca.* 200 μg.) in alcohol (1 ml.) was hydrolysed with 1% hydrochloric acid (1 ml.) at 100° for 10 min. The mixture was cooled, applied as a streak on Whatman's No. 3 paper, and separated in the normal manner. After elution, the intermediate monoside was identified in the usual way (Tables 2 and 3).

*Determination of the Relative Concentration of the Different Components.*—The original extract (2 ml.) was separated as described and the individual flavones were hydrolysed with 2N-hydrochloric acid (2 ml.) for 1 hr. and made up with alcohol to 50 ml. The aglycone concentration in each component was determined spectrophotometrically. The anthocyanin in band 6 was estimated after elution as cyanin.

*Preparation of Reference Compounds.*—All the flavones required for this investigation, except those described below, were prepared by recorded methods.

4′-*Hydroxy*-3′ : 5 : 7-*trimethoxyflavone.* Condensation of 2 : 4-di-*O*-methylphloracetophenone (2·9 g.) with 4-*O*-benzylvanillin (3·6 g.) in ethanol (40 ml.) in the presence of sodium hydroxide (5 g. in water, 5 ml.) overnight yielded 4-*benzyloxy*-2′-*hydroxy*-3 : 4′ : 6′-*trimethoxychalkone* (2·9 g.). This recrystallised from alcohol in bright yellow plates, m. p. 134·5—136°, giving a brown colour with ferric chloride in alcohol (Found : C, 71·7; H, 5·7. $C_{25}H_{24}O_6$ requires C, 71·4; H, 5·8%). The chalkone (2·5 g.) was dehydrogenated with selenium dioxide (2·5 g.) in boiling amyl alcohol (40 ml.) during 18 hr. and after filtration the solvent was removed in steam. The resultant dark solid (1·1 g.) was recrystallised from aqueous acetic acid, yielding cream-coloured needles of 4′-*benzyloxy*-3′ : 5 : 7-*trimethoxyflavone*, m. p. 208—209° (Found : C, 68·6, 68·6 H, 5·1, 5·5. $C_{25}H_{22}O_6,2H_2O$ requires C, 68·8; H, 5·5%). The benzyloxyflavone (0·9 g.) was hydrolysed with acetic acid (7 ml.) and concentrated hydrochloric acid (5 ml.) for 1 hr. at 100°. After steam-distillation and recrystallisation from alcohol, 4′-*hydroxy*-3′ : 5 : 7-*trimethoxyflavone* was obtained as pale yellow needles, m. p. 223—224° (0·6 g.) (Found : C, 62·0;H, 5·4. $C_{18}H_{16}O_6,H_2O$ requires C, 61·9; H, 5·8%).

3′-*Hydroxy*-4′ : 5 : 7-*trimethoxyflavone.*—A solution of 2 : 4-di-*O*-methylphloracetophenone (2·2 g.), 3′-*O*-benzyl*iso*vanillin (2·7 g.) in alcohol (30 ml.) was treated with sodium hydroxide (4 g. in water, 4 ml.) overnight, yielding 3-*benzyloxy*-2′-*hydroxy*-4 : 4′ : 6-*trimethoxychalkone* (2·6 g.), which gave lemon-yellow needles (from alcohol), m. p. 106—107° (Found : C, 70·9; H, 6·1. $C_{25}H_{24}O_6$ requires C, 71·4; H, 5·8%).

This compound (1·8 g.) was dehydrogenated as before, yielding 3′-*benzyloxy*-4′ : 5 : 7-*trimethoxyflavone*, cream-coloured needles (from alcohol), m. p. 190—191° (Found : C, 71·2; H, 5·4. $C_{25}H_{22}O_6$ requires C, 71·8; H, 5·3%). This material (0·9 g.) was debenzylated with acetic acid and concentrated hydrochloric acid as before and the product on recrystallisation from alcohol gave 3′-*hydroxy*-4′ : 5 : 7-*trimethoxyflavone* as buff-coloured needles, m. p. 230—231° (Found : C, 65·0; H, 5·1. $C_{18}H_{16}O_6$ requires C, 65·5; H, 5·5%).

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## 556. *Polynuclear Heterocyclic Systems. Part VII.* Syntheses using the Elbs Reaction.*

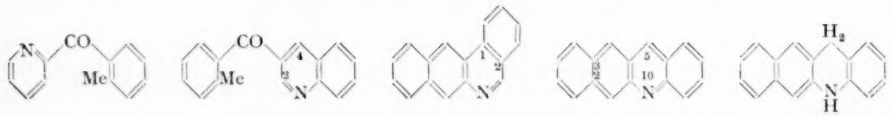
By G. M. Badger and R. Pettit.

Three aryl pyridyl ketones and two aryl quinolyl ketones have been prepared and pyrolysed according to Elbs's method. In three cases extensive decomposition took place and no pure product could be isolated; but 3-*o*-toluoylquinoline (II) gave 5 : 10-dihydro-2 : 3-benzacridine (V), and 2-(2-methyl-1-naphthoyl)pyridine (VI) gave 9-hydroxy-8-aza-1 : 2-benzanthracene (VII).

The mechanism of the Elbs reaction is discussed and a free-radical mechanism is proposed.

The Elbs reaction has been extensively used for the preparation of polycyclic aromatic hydrocarbons. It involves the elimination of water from an *o*-methyldiaryl ketone by pyrolysis; although the yields are often poor, this is usually offset by the ready availability of the intermediate ketones. Little use has so far been made of this reaction for the preparation of polynuclear heterocyclic compounds, although Fieser and Hershberg (*J. Amer. Chem. Soc.*, **1940**, **62**, 1640) have prepared 4'-aza-1 : 2-benzanthracene from 7-methyl-4-indanyl 5-quinolyl ketone. The reaction has, however, been made to provide a number of polycyclic derivatives of thiophen (Buu-Hoï and Hoán, *Rec. Trav. chim.*, 1948, **67**, 309). Two carbazole derivatives have also been prepared by pyrolysis of 3-aroyl-2-methylindoles, but several ketones of this type underwent extensive decomposition and gave tars (Buu-Hoï, Hoán, and Khôi, *J. Org. Chem.*, 1950, **15**, 131). These few examples all involved cyclisation into a carbocyclic ring, and there seems to have been no attempt to investigate the possibility of cyclisation into a ring containing a hetero-atom. The work now reported was undertaken in order to examine the possibilities of the method in this field and, at the same time, the mechanism of the reaction.

Three aryl pyridyl ketones and two aryl quinolyl ketones have been prepared, and it was hoped that these would undergo cyclisation into the heterocyclic ring to give aza-anthracenes or aza-benzanthracenes. Success was, however, limited. Water certainly was evolved on pyrolysis of 2-*o*-toluoylpyridine (I), but owing to extensive decomposition no pure product could be isolated. Similarly, no pure product could be isolated after pyrolysis of 3-(2-methyl-1-naphthoyl)pyridine and of 4-*o*-toluoylquinoline.



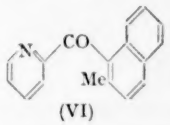

(I) (II) (III) (IV) (V)

3-*o*-Toluoylquinoline (II) might undergo cyclisation at the 2- or the 4-position and yield 4-aza-1 : 2-benzanthracene (III) or 2 : 3-benzacridine (IV) respectively. In fact, the former took place and 5 : 10-dihydro-2 : 3-benzacridine (V) was isolated in 10% yield. It was identified by oxidation to 2 : 3-benzacridone.

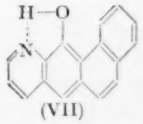
Pyrolysis of 2-(2-methyl-1-naphthoyl)pyridine (VI) gave a complex mixture from which a yellow crystalline compound was isolated. Although this contained one oxygen atom, it was insoluble in sodium hydroxide solution, was unaffected by zinc dust and boiling acetic anhydride, and could not be acetylated or benzoylated. It is suggested that it is 9-hydroxy-8-aza-1 : 2-benzanthracene (VII, or the tautomer, VII*a*), and that it was formed from the ketone (VI) by dehydrogenation rather than by dehydration. Such a compound would exhibit strong hydrogen-bonding between the hydroxyl group and the hetero-atom. Indeed, the pronounced conjugation between the hydroxyl group and the

* Part VI, *J.*, 1952, 1877.

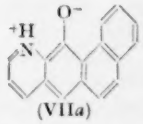
*meso*-position which would occur in such a structure would tend to make the hydrogen bond a very strong one, and hence depress all the hydroxyl group reactions (such as alkali solubility). As is well known, *o*-hydroxyazobenzenes are insoluble in alkali and can be acylated only with great difficulty.



(VI)



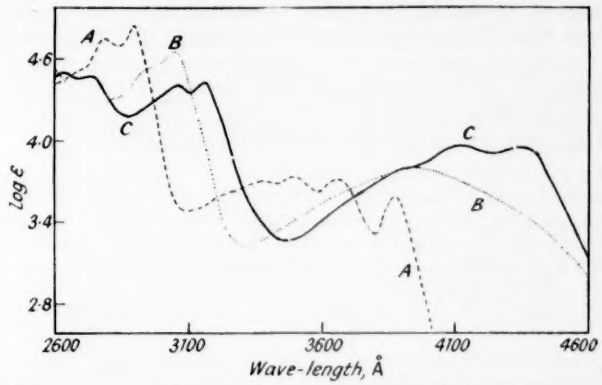
(VII)



(VII*a*)

The absorption spectrum of 9-hydroxy-8-aza-1 : 2-benzanthracene was unexpectedly different from that of 5-aza-1 : 2-benzanthracene (Badger, Pearce, and Pettit, *J.*, 1951, 3199) (see Figure), probably because the hydroxy-compound exists largely in the tauto-

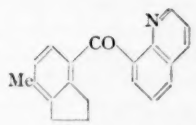
*Absorption spectra of aza-benzanthracenes.*

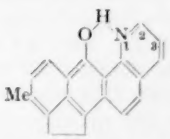



*A*, 5-*Aza*-1 : 2-*benzanthracene in ethanol* (Badger, Pearce, and Pettit, *loc. cit.*).
*B*, 5-*Aza*-1 : 2-*benzanthracene in alcoholic hydrochloric acid* (*prepared by diluting concentrated hydrochloric acid with alcohol to give a solution containing* 7·5% *of hydrogen chloride*).
*C*, 9-*Hydroxy*-8-*aza*-1 : 2-*benzanthracene in ethanol.*

meric form (VII*a*) in ethanol. This conclusion is strongly supported by the fact that its absorption spectrum *in ethanol* very closely resembles that of 5-aza-1 : 2-benzanthracene in *alcoholic hydrochloric acid*. The latter solution must contain the 5-aza-1 : 2-benzanthracene cation, and this structure very closely resembles the ionic form (VII*a*).

Fieser and Hershberg (*loc. cit.*) obtained an oxygenated compound having rather similar properties by pyrolysis of 7-methyl-4-indanyl 8-quinolyl ketone (VIII), and a similar hydrogen-bonded structure (IX) was proposed for it. They pointed out that the absorption spectrum of this substance (not reproduced by them) did not resemble that of the analogous substance, 20-methyl-4-azacholanthrene; the present work suggests that it may resemble that of the 20-methyl-4-azacholanthrene cation.

(VIII)


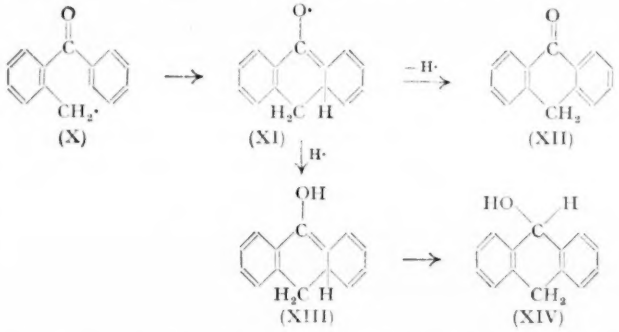
(IX)

The various heterocyclic ketones used in this investigation were prepared by condensing *o*-tolylmagnesium bromide or 2-methyl-1-naphthylmagnesium bromide with a cyanopyridine or cyanoquinoline. The resulting complexes were generally decomposed by boiling hydrochloric acid, and the required ketones obtained directly and in good yield. In a few cases

in which decomposition with ammonium chloride was attempted, the intermediate ketimines were isolated; these were hydrolysed to the ketones by boiling acid.

*Mechanism of the Elbs Reaction.*—Very little is known about the mechanism of the Elbs reaction (see, however, Fieser, "The Chemistry of Natural Products related to Phenanthrene," Reinhold Publ. Corp., New York, 2nd edn., p. 107; "Organic Reactions," 1942, Vol. I, p. 129), and none of the suggested mechanisms is completely satisfactory. Anthrones have often been obtained as by-products and have sometimes been the chief products (Morgan and Coulson, *J.*, 1931, 2323). It is difficult to explain their formation unless the intermediate dihydroanthranols undergo oxidation rather than dehydration, and this seems extremely unlikely. Moreover, Campbell, Marks, and Reid (*J.*, 1950, 3466) found that the pyrolysis of 4-*o*-toluoylfluoranthene gives some 4 : 5-*o*-xylylenefluoranthene as well as some of the expected product and it is difficult to see how the xylylene compound could arise by any mechanism involving addition to a diene system.

No catalyst has been found for the Elbs reaction, and the high temperature necessary suggests that it may be of free-radical nature. For these and other reasons, the following modification of the Fieser–Dietz mechanism is proposed. It is suggested that the first step is loss of a hydrogen atom from the activated methyl group to give a radical such as (X). Intramolecular substitution would give the intermediate (XI, and resonance structures) which could either lose a hydrogen atom to yield anthrone (XII) or undergo reduction to (XIII) and rearrangement to dihydroanthranol (XIV).




The nature of the ketone evidently determines which route is favoured, although both probably occur to some extent in most cases. Some of the anthrone formed might undergo reduction with two atoms of hydrogen to give dihydroanthranol, but the work of Hurd and Azorlosa (*J. Amer. Chem. Soc.*, 1951, **73**, 37) indicates that this route cannot be of great importance. Incidentally, the above mechanism satisfactorily accounts for the formation of hydroxy-aza-compounds (such as VII and IX), the intermediate being stabilised by hydrogen-bonding.

Although the evidence is still inconclusive there are several facts which support a free-radical mechanism. The presence of free hydrogen atoms during the reaction is supported by the fact that dihydro-aromatic compounds are often formed: pyrolysis of 4 : 6-dibenzoyl-1 : 3-xylene, for example, gives dihydropentacene as the major product (Clar and John, *Ber.*, 1929, **62**, 3021; 1931, **64**, 981); and in the present work 5 : 10-dihydro-2 : 3-benzacridine (V) was obtained by pyrolysis of (II). Finally, various by-products have been obtained in certain Elbs reactions which can only have been formed by decomposition of the ketones into free radicals and reduction with hydrogen atoms. Phenanthrene has been obtained from an aryl phenanthryl ketone (Fieser and Dietz, *loc. cit.*), anthracene from an anthryl aryl ketone (Clar, John, and Hawran, *Ber.*, 1929, **62**, 940), and 2-methylnaphthalene from 1-benzoyl-2-methylnaphthalene (present work). Pyrolysis of the last compound also gave some benzaldehyde; and benzoic acid and benzaldehyde have been detected on pyrolysis of 1 : 5-dibenzoyl-2 : 6-dimethylnaphthalene (Clar, Wallenstein, and Avenarius,

*Ber.*, 1929, **62**, 950). The formation of all these products is consistent with the view that the ketone undergoes homolytic fission to some extent and that the fragments are reduced by hydrogen atoms.

## Experimental

2-o-*Toluoylpyridine* (I).—To a Grignard solution from *o*-bromotoluene (37·5 g.), magnesium (5·3 g.), and anhydrous ether (150 c.c.), benzene (50 c.c.) was added, and the mixture distilled until the temperature rose to 55°. To the cooled mixture, a solution of 2-cyanopyridine (15 g.) [prepared from 2-aminopyridine (*Org. Synth.*, 1946, **26**, 16) by Craig's method (*J. Amer. Chem. Soc.*, 1934, **56**, 231)] in anhydrous benzene (50 c.c.) was slowly added with constant stirring. The mixture was then refluxed for 8 hr. (cf. Fieser and Bowen, *J. Amer. Chem. Soc.*, 1940, **62**, 2103), then poured on ice (200 g.) and ammonium chloride (160 g.), and the whole was refluxed for 2 hr. During this time the ether was removed. The aqueous solution was then discarded, the crude product taken up in benzene, and the benzene solution dried and evaporated. After distillation under reduced pressure (b. p. 180—200°/12 mm.) and crystallisation from light petroleum, 2-o-*toluoylpyridine* (12·0 g.) was obtained as colourless prisms, m. p. 69—70° (Found: C, 79·4; H, 5·7; N, 7·2. $C_{13}H_{11}ON$ requires C, 79·2; H, 5·6; N, 7·1%). The *picrate* formed yellow needles, m. p. 122—124°, from ethanol (Found: C, 53·45; H, 3·3. $C_{19}H_{14}O_8N_4$ requires C, 53·5; H, 3·3%).

2-(2-*Methyl*-1-*naphthoyl*)*pyridine*.—A Grignard solution from 1-bromo-2-methylnaphthalene (106·3 g.) (Adams and Binder, *J. Amer. Chem. Soc.*, 1941, **63**, 2773), magnesium (11 g.), anhydrous ether (300 c.c.), and anhydrous benzene (200 c.c.) was treated as above with 2-cyanopyridine (25 g.) in anhydrous benzene (200 c.c.) at 5°. Next morning the mixture was refluxed for 1 hr., cooled, and poured on ice (300 g.). Concentrated hydrochloric acid (100 c.c.) was added, and the mixture steam-distilled for 5 hr. The aqueous phase was discarded, and aqueous ammonia added to the residue. The product was taken up in chloroform (300 c.c.), and the solution washed and evaporated. After recrystallisation of the residue from light petroleum, 2-(2-*methyl*-1-*naphthoyl*)*pyridine* (39·5 g.) was obtained as colourless prisms, m. p. 126—128° (Found: C, 82·9; H, 5·4; N, 5·9. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3; N, 5·7%). The *picrate* formed yellow needles, m. p. 143—146°, from benzene (Found: C, 57·6; H, 3·65. $C_{17}H_{13}ON,C_6H_3O_7N_3$ requires C, 58·0; H, 3·4%).

In a preliminary run, the hydrolysis of the complex was attempted with ammonium chloride instead of hydrochloric acid. Hydrolysis was incomplete and the product was 2-*methyl*-1-*naphthyl* 2-*pyridyl ketimine*. It crystallised from light petroleum in colourless prisms, m. p. 84—86° (Found: C, 83·1; H, 5·8; N, 10·85. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7; N, 11·4%). The *picrate* crystallised from ethanol in yellow prisms, m. p. 191—193° (Found: C, 58·2; H, 3·6. $C_{23}H_{17}O_7N_5$ requires C, 58·1; H, 3·6%). Hydrolysis with boiling alcoholic hydrochloric acid for 5 hr. gave 2-(2-methyl-1-naphthoyl)pyridine.

3-(2-*Methyl*-1-*naphthoyl*)*pyridine* (VI).—As in the previous experiment a Grignard solution from 1-bromo-2-methylnaphthalene (106·3 g.) was treated with 3-cyanopyridine (25 g.) (Adkins, Wolff, Pavlic, and Hutchinson, *J. Amer. Chem. Soc.*, 1944, **66**, 1293) in benzene (250 c.c.), at 5°, the mixture refluxed for 3 hr., and the yellow precipitate collected and added to crushed ice (200 g.). Concentrated hydrochloric acid (100 c.c.) was then added and the mixture steam-distilled for 4 hr., additional concentrated hydrochloric acid (100 c.c.) being added at half-hourly intervals. The aqueous solution was then discarded and the dark viscous material taken up in ether, washed with aqueous ammonia, and filtered. After drying, the ether was evaporated and the 3-(2-*methyl*-1-*naphthoyl*)*pyridine* distilled (b. p. 200—210°/14 mm.). It then crystallised during several weeks, and was recrystallised from light petroleum as prisms (22·5 g.), m. p. 97—98° (Found: C, 82·9; H, 5·5; N, 5·8. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3; N, 5·7%). The *picrate* crystallised from ethanol in yellow prisms, m. p. 183—184° (Found: C, 58·2; H, 3·2. $C_{23}H_{16}O_8N_4$ requires C, 58·0; H, 3·4%).

Use of ammonium chloride as above gave 2-*methyl*-1-*naphthyl* 3-*pyridyl ketimine*, prisms (from light petroleum), m. p. 97—98° (Found: C, 83·1; H, 5·6; N, 10·85. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7; N, 11·4%).

3-*Cyanoquinoline*.—3-Bromoquinoline was prepared essentially as described by Claus and Collischonn (*Ber.*, 1886, **19**, 2763), except that 48% hydrobromic acid was used as solvent instead of ether, and gave 3-cyanoquinoline on treatment with cuprous cyanide by Gilman and Spatz's method (*J. Amer. Chem. Soc.*, 1941, **63**, 1553).

3-o-*Toluoylquinoline* (II).—A Grignard solution prepared from *o*-bromotoluene (66·6 g.), magnesium (9·4 g.) and anhydrous ether (300 c.c.) was added to a solution of 3-cyanoquinoline

(30 g.) in anhydrous benzene (250 c.c.), at 0°. The mixture was then stirred at 0° for an hr., refluxed for a further hr., and poured on crushed ice (200 g.). Concentrated hydrochloric acid (100 c.c.) was added, and the mixture steam-distilled for 4 hr. After cooling, the viscous residue was made alkaline with aqueous ammonia, dissolved in ether, and extracted with concentrated hydrochloric acid (3 × 100 c.c.). The acid extracts were made alkaline with ammonia, the liberated product taken up in ether, the ether evaporated and the residue distilled (b. p. 215—230°/14 mm.). The resulting pale yellow viscous oil (20 g.) solidified during several weeks and was recrystallised from light petroleum. 3-o-*Toluoylquinoline* formed plates, m. p. 80·5—81·4° (Found: C, 82·85; H, 5·3; N, 5·7. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3; N, 5·8%). The *picrate* crystallised from ethyl acetate in yellow plates, m. p. 209—210° (Found: C, 58·2; H, 3·4; N, 11·6. $C_{23}H_{16}O_8N_4$ requires C, 58·0; H, 3·4; N, 11·8%).

4-o-*Toluoylquinoline*.—A solution of *o*-tolylmagnesium bromide (76 g.) in anhydrous ether (250 c.c.) was added with constant stirring to a solution of 4-cyanoquinoline (30 g.) (Hamer, *J.*, 1939, 1008), in benzene (200 c.c.), at 5°, stirred for 1 hr., and gently refluxed for a further hr. It was then poured on crushed ice (200 g.), concentrated hydrochloric acid (100 c.c.) added, and the mixture steam-distilled for 4 hr. The residual tarry material was dissolved in ether, and washed several times with dilute aqueous ammonia, the ether evaporated off, and the product distilled (b. p. 195—215°/0·5 mm.). The resulting viscous 4-o-*toluoylquinoline* (30 g.) slowly crystallised and recrystallised from light petroleum as prisms, m. p. 63—64·5° (Found: C, 82·9; H, 5·5; N, 5·8%). The *picrate* crystallised from ethanol in bright yellow plates, m. p. 191—192° (Found: C, 58·4; H, 3·8; N, 11·2%).

*Pyrolysis of the Ketones*.—(i) Preliminary experiments were carried out on the pyrolysis of 1-benzoyl-2-methylnaphthalene under a variety of conditions. The fore-run obtained on pyrolysis at 360° for 7 hr. contained benzaldehyde (identified as the 2 : 4-dinitrophenylhydrazone) and 2-methylnaphthalene (identified as the picrate). Extraction of the residue with benzene and chromatography on alumina gave 0·75 g. of 1 : 2-benzanthracene.

(ii) 2-(2-Methyl-1-naphthoyl)pyridine (5 g.) was heated in a small distillation flask in a metal-bath at 280°. After 2 hr. evolution of water had ceased, and the residue was distilled at 1 mm. Alcohol (2 c.c.) was added to the dark red viscous distillate, and the solid which separated (0·5 g.) was collected. After recrystallisation from benzene 9-*hydroxy*-8-*aza*-1 : 2-*benzanthracene* formed yellow needles, m. p. 184·5—185·5° (Found: C, 83·4; H, 4·4; N, 5·8. $C_{17}H_{11}ON$ requires C, 83·25; H, 4·5; N, 5·7%). It dissolved in alcohol, benzene, and chloroform to give yellow solutions with a yellow-green fluorescence.

(iii) 3-*o*-Toluoylquinoline (5 g.) was heated at 380—400° for 4 hr. The residue was distilled at 1 mm., and the dark red, viscous distillate triturated with alcohol. The resulting solid was collected (0·5 g.), and after recrystallisation from chloroform 5 : 10-dihydro-2 : 3-benzacridine formed colourless needles, m. p. 285° (rapid heating) (Found: C, 88·4; H, 5·7; N, 6·2. Calc. for $C_{17}H_{13}N$: C, 88·3; H, 5·7; N, 6·1%). It also crystallised from benzene in pale orange plates, m. p. 285° (rapid heating).

Oxidation with potassium dichromate in boiling glacial acetic acid followed by sublimation of the product and recrystallisation from glacial acetic acid gave 2 : 3-benzacridone as orange-yellow, m. p. 304° in agreement with the literature (Schöpff, *Ber.*, 1893, **26**, 2589).

(iv) The remaining ketones were pyrolysed under a variety of different conditions of time and temperature. Water was invariably evolved, and a small yield of a dark viscous oil was obtained on distillation. No pure product could, however, be isolated.

*Absorption Spectra*.—These were determined with a Hilger Uvispek spectrophotometer.

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

UNIVERSITY OF ADELAIDE. [*Received, January 23rd*, 1953.]

## 557. *The Conductivity of Potassium Chloride in Mixed Solvents.*

By J. Daly and C. G. Smith.

The conductivities of potassium chloride in mixtures of water with dioxan, acetone, or *iso*propanol as solvent have been determined. Theoretical and experimental Onsager slopes have been compared for the different dielectric constants. At dielectric constants above 60, the experimental Onsager slopes approach the theoretical slopes from above, whereas at dielectric constants below 50—60, the reverse occurs, suggesting that, at dielectric constants of this order, the onset of ion association first becomes apparent. The conductivities of solutions of constant electrolytic concentration were plotted against the dielectric constant. The results are considered from the point of view of solvation and the change in dielectric constant.

A new type of cell is described, together with a high-sensitivity detector and oscillator unit. A modified Jones and Joseph's bridge was employed.

In recent years conductance measurements of many electrolytes in mixed solvents have been reported. Variations of conductance in these media have been accounted for satisfactorily by Bjerrum's ion-pair treatment, on a basis of variation of dissociation constants with change in the dielectric constant. Apart from the work of James (*J.*, 1950, 1094; 1951, 153, 2925), the majority of measurements appear to have been made with large ions, where no definite "solvent effect" has been encountered, as those large ions have presumably no solvation sheath. Comparative measurements employing different solvent media do not appear to have been carried out. In the present investigation, a simple uni-univalent electrolyte (potassium chloride) was used in three mixed solvents. The choice of dioxan, acetone, and *iso*propanol was determined by the desire to differentiate between the effect of dielectric-constant lowering and that due to the specific effect of the non-aqueous additions.

### Experimental

*The Bridge.*—The Wagner ground was connected as suggested by Luder (*J. Amer. Chem. Soc.*, 1940, **62**, 89) to a modified Jones and Joseph's bridge (*ibid.*, 1928, **50**, 1049). The bridge components were shielded, and all the leads were screened, including those from the detector. In order to eliminate possible sources of eddy currents, the screening was connected to a common earth. The Wagner ground was fixed for given values of the ratio arms, resetting being unnecessary.

*Detector.*—The majority of detectors lack sensitivity at the higher resistance ranges, and since high resistances were being measured, a detector unit of the visual indicator type was used (Fig. 1). After amplification, by use of a high-gain valve $V_1$ (6J7), the signal was rectified, and fed to the grid of $V_2$ (6J5), which formed one arm of a direct-current bridge. Stability was improved by employing negative feed-back, the second arm of the bridge being used as the feedback resistance. Input to the amplifier was transformer-coupled. This enabled the detector to have a common chassis with that of the oscillator. A sensitivity potentiometer controlled the gain of the detector when the bridge was off balance. Zero control regulated the setting of the galvanometer needle on a suitable part of the scale. At maximum sensitivity the galvanometer needle indicated a variation of 1 ohm in 300,000.

*Oscillator.*—An oscillator (Fig. 2) capable of producing a good sinusoidal wave at the selected frequency was assembled from standard components. It was of the true Wien bridge type, consisting of a two-valve amplifier with feed-back through a resistance–capacitance network. This provided a rapid change of phase with frequency, giving positive feed-back, and hence causing oscillations at a fixed frequency. The frequency was varied from 300 to 5000 cycles per sec., by altering the resistance–capacitance network on five ranges. Negative feed-back was provided through a thermistor to give a pure sinusoidal wave-form. The oscillator was coupled to a small-power valve (6F6) operated as a cathode follower, the output being taken from the cathode through a potentiometer and transformer.

*Conductivity Cell.*—Jones and Bollinger (*J. Amer. Chem. Soc.*, 1931, **53**, 411) indicated that the Parker effect (Parker, *ibid.*, 1923, **45**, 1366, 2017) can be eliminated by arranging the contact arms and the filling tubes of the cell as far apart as possible. The cell (Fig. 3) was intended

to reduce this error still more, by employing only one filling tube. It could be used outside the cell, shorter leads to the bridge being then possible. Quick emptying and filling of the cell was facilitated. The cell was of Pyrex glass. The electrodes, 5 cm. apart, were backed with glass, and sealed into the walls, contact being made to the bridge through mercury cups.

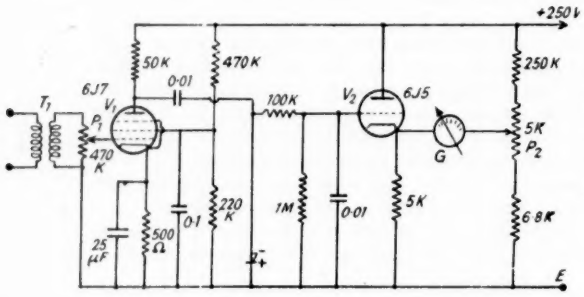



FIG. 1. *Circuit diagram of detector unit.*

$T_1$. Intervalve transformer (3 : 1).
$P_1$. Sensitivity control.
$P_2$. Zero-set potentiometer.

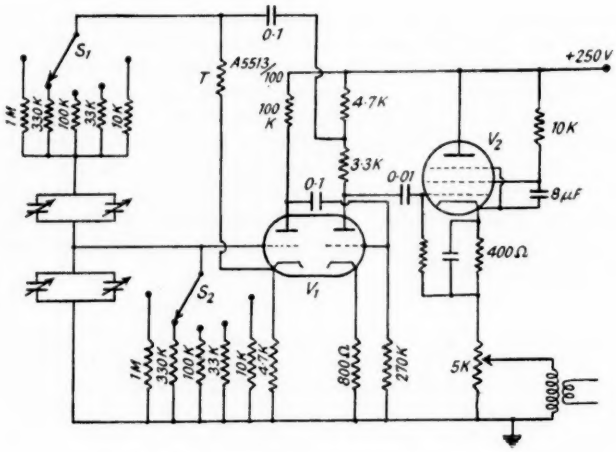
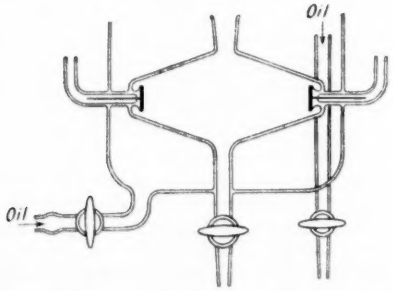



FIG. 2.

$V_1$. 6SN7.
$V_2$. 6F6.
$T$. Thermistor A5513/100.
The resistance and capacitance, shown to the right of $V_1$, are 270K and 25μF, respectively.

FIG. 3.




Surrounding the cell was a jacket through which oil was circulated from a thermostatic reservoir, by means of a rotary pump. The temperature of the solution in the cell was read directly from a thermometer, the presence of which in the cell did not interfere with the resistance of the solution being measured. Blacked electrodes were used in all measurements.

*Thermostat.*—This was of standard design, and a high-grade paraffin served as the thermostatic liquid. Measurements were made at 25° ± 0·05°. The thermostat was in operation continually, but when measurements were not actually being recorded, the stirring motor was switched in parallel with the heater.

*Purification of Solvents and Solute.—Conductivity water.* Water used in all measurements was prepared from a Pyrex still by fractional distillation in a counter-current of pure nitrogen (Vogel and Jeffrey, *J.*, 1931, 1201). The water was stored in well-seasoned flasks under nitrogen, and had a specific conductance of not more than $0{\cdot}5 \times 10^{-6}$ mho cm.$^{-1}$.

*Dioxan.* Commercial 1 : 4-dioxan was purified by Vogel's method (" Practical Organic Chemistry," Longmans Green and Co., London, 1948, p. 175). Physical constants are here compared with literature values (Ibert Mellan, " Industrial Solvents," Reinhold Publ. Corp., New York, 1950, 2nd edn. p. 674); given in parentheses: b. p. 101·5°/760 mm. (101·3°/760 mm.), $n_D^{20}$ 1·4220 (1·4221), $d_{20}^{20}$ 1·0482 (1·0356), $\kappa$—($2 \times 10^{-8}$ mho).

*Acetone.* " AnalaR " acetone was refluxed over anhydrous copper sulphate, kept for 24 hr. over fresh anhydrous copper sulphate, and fractionally distilled. Its physical constants are compared here with literature values (*op. cit.*, p. 589): b. p. 56·1°/760 mm. (56·1°/760 mm.), $n_D^{20}$ 1·3590 (1·3584), $d_{20}^{20}$ 0·7971 (0·790—0·793), $\kappa$—($6 \times 10^{-8}$ mho).

iso*Propanol.* A batch of *iso*propanol was kept over freshly fired quicklime for 48 hr. and then fractionated. Distillate of b. p. 82—84° was further distilled from sodium at 82·4°. The constants are here compared with recorded values (*op. cit.*, p. 476): b. p. 82·4°/759 mm. (82·4°/760 mm.), $n_D^{20}$ 1·3778 (1·3776), $d_{20}^{20}$ 0·7875 (0·7874), $\kappa$—$3{\cdot}5 \times 10^{-7}$ mho).

*Potassium chloride.* A stock sample of " AnalaR " salt was crystallised twice from freshly distilled water, and twice from conductivity water. It was then heated to dull redness in a platinum crucible, powdered, and kept in a thermostatic oven at 180° for 2 days. After spectroscopic examination, the stock was stored in a desiccator.

*Determination of Cell Constant.*—Shedlovsky's equivalent conductance data (*Trans. Electrochem. Soc.*, 1937, **66**, 165) and those of Davies (*J.*, 1937, 432) were used to calculate the cell constant, over a range of potassium chloride concentrations.

*Conductivity Measurements in Mixed Solvents.*—The determination of the conductance of the various solvents was followed immediately by conductance measurements with potassium chloride as the electrolyte. The results are tabulated, the equivalent conductance being corrected for that of the solvent. No difficulties were experienced in measurements with water–acetone and water–*iso*propanol, but during the water–dioxan measurements, fluctuations arose which were attributed to the formation of air bubbles.

Dielectric-constant data are taken from Akerlöf (*J. Amer. Chem. Soc.*, 1932, **54**, 4125) and Wyman and Ingalls (*ibid.*, 1936, **58**, 1241), and viscosity data are due to Geddes (*ibid.*, 1933, **55**, 4832) and Owen and Waters (*ibid.*, 1938, **60**, 2371). Viscosity measurements of *iso*propanol–water mixtures, carried out with a constant-pressure Ostwald viscometer, agreed with Whitman and Hurst's data (*ibid.*, 1930, **52**, 4766). The conductances of the pure solvents were not taken, but the literature values appear under physical constants for each solvent.

## Discussion

Conductivity data for potassium chloride in mixed solvents appear in Tables 1, 2, and 3. The dielectric constants of these media were chosen (by varying the concentrations of the non-aqueous additions) such that they were of comparable values. In Figs. 4, 5, and 6, both experimental and theoretical Onsager slopes have been obtained by using the equation for uni-univalent electrolytes as simplified to

$$\Lambda_0 - \Lambda = \sqrt{c}\left[\frac{158{\cdot}34}{D^{\frac{3}{2}}}\Lambda_0 + \frac{2{\cdot}3706}{D^{\frac{1}{2}}\eta}\right]$$

This use of the equation presupposes that the non-aqueous additions introduce no alteration in the mobilities other than those accounted for by changes in dielectric constant and viscosity. The values of $\Lambda_0$ have been obtained from large-scale plots of $\Lambda$ against the square-root of the electrolyte concentration. Onsager (*Physikal. Z.*, 1927, **28**, 277) pointed out that completely dissociated electrolytes should approach the limiting slope asymptotically from above, whereas incompletely dissociated electrolytes should approach from below. At dielectric constants within the range of 50—60, it has been experimentally established that ion-association occurs, which is in agreement with Bjerrum's treatment (*Chem. Reviews*, 1935, **17**, 227). However, the dielectric-constant value at which ion-association occurs, varies in each medium.

In Fig. 7, the curves of equivalent conductances against the dielectric constant for each solvent medium exhibit a characteristic limiting slope. *iso*Propanol–water solvents

cause most depression of the equivalent conductance (with respect to water as solvent), and dioxan–water solvents least, acetone–water being intermediate in value. Davies and Monk (*J.*, 1951, 2719), investigating the dissociation constants of silver acetate against changing dielectric constant, also found variations which were attributed to the nature of the solvent, and suggested that the effect may be explained by supposing that water molecules are being replaced in the solvation sheath of the ion by the organic solvent

FIG. 4. *Dioxan–water media.*

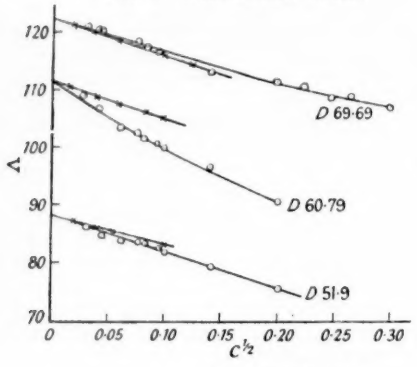
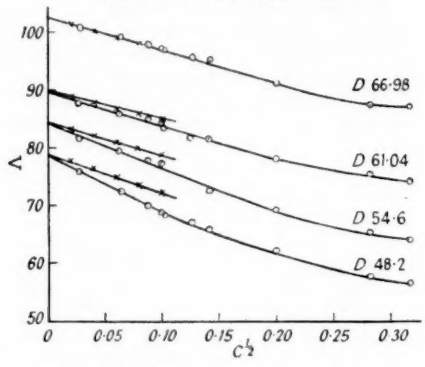
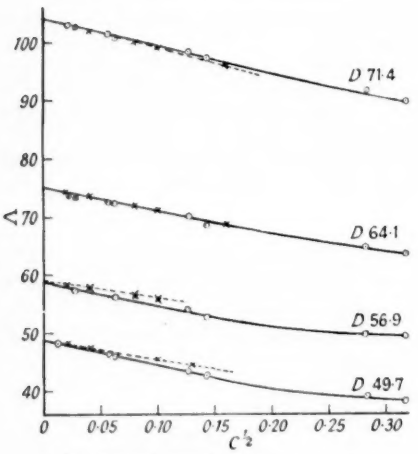



FIG. 5. *Acetone–water media.*



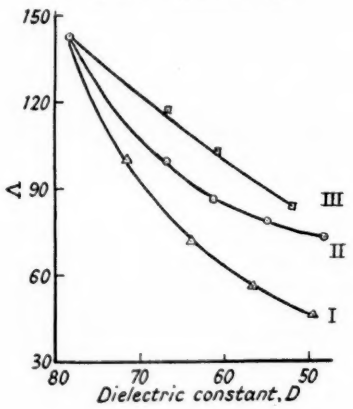

○ Experimental. × Theoretical (Onsager slopes).

FIG. 6. iso*Propanol–water media.*




○ Experimental.
× Theoretical (Onsager slopes).

FIG. 7. *Plot of equivalent conductance against dielectric constant (0·004*N*-KCl solution).*




I. *iso*Propanol–water.
II. Acetone–water.
III. Dioxan–water.

molecules. The latter workers report that, where silver acetate was used as the electrolyte, Walden's product, $\Lambda_0\eta$ remained approximately constant.

In this investigation, with the lower concentrations of non-aqueous additions, the values of $\Lambda_0\eta$ approximate to that of water, as solvent medium, but with higher non-aqueous concentrations $\Lambda_0\eta$ shows considerable variations. Values of $\Lambda_0$, $\eta$, and $\Lambda_0\eta$ are tabulated in Table 4. According to Stokes's law, an electric force $XZe$ acting on a spherical ion of radius $r$, would maintain it at a velocity $v = XZe/6\pi\eta r$, where $\eta$ is the viscosity of the medium. If it is assumed that a solvated ion moves as a single entity under an applied potential, then Stokes's law will give a direct measure of the primary solvation sheath

(Bockris, *Quart. Reviews*, 1949, **3**, 173). The variation of $\Lambda_0\eta$ in the different media can then be accounted for by a change in the ionic radius (caused by a change in the solvation sheath) which introduces a change in the velocity of the ion in different media. This can only occur by the organic solvent entering the solvation sheath, which is Debye's " salting effect " (Debye and McAulay, *Physikal. Z.*, 1925, **26**, 22). When an electrolyte is dissolved in a mixture of water and an organic solvent, the ions (particularly the cation)

TABLE 1. iso*Propanol–water media.*

| | 10% | 20% | 30% | 40% | | 10% | 20% | 30% | 40% |
|---|---|---|---|---|---|---|---|---|---|
| $10^6\kappa$, mho | 1·657 | 1·13 | 0·92 | 0·74 | $10^6\kappa$, mho | 1·657 | 1·13 | 0·92 | 0·74 |
| *D* | 71·4 | 64·1 | 56·9 | 49·7 | *D* | 71·4 | 64·1 | 56·9 | 49·7 |
| Concn., N | Λ | Λ | Λ | Λ | Concn., N | Λ | Λ | Λ | Λ |
| 0·10 | 89·53 | 63·30 | 49·19 | 38·22 | 0·0032 | 101·44 | 72·15 | 55·98 | 46·74 |
| 0·08 | 91·25 | 64·53 | 49·44 | 39·27 | 0·0008 | 102·33 | 73·02 | 57·05 | — |
| 0·02 | 96·89 | 67·86 | 52·77 | 42·91 | 0·00064 | 102·72 | 73·51 | — | — |
| 0·016 | 98·10 | 69·82 | 54·10 | 43·69 | 0·00016 | — | — | — | 48·47 |
| 0·004 | 100·39 | 71·91 | 56·11 | 45·61 | | | | | |

TABLE 2. *Acetone–water media.*

| | 20% | 30% | 40% | 50% | | 20% | 30% | 40% | 50% |
|---|---|---|---|---|---|---|---|---|---|
| $10^6\kappa$, mho | 1·92 | 1·76 | 1·65 | 0·74 | $10^6\kappa$, mho | 1·92 | 1·76 | 1·65 | 0·74 |
| *D* | 66·98 | 61·04 | 54·6 | 48·2 | *D* | 66·98 | 61·04 | 54·6 | 48·2 |
| Concn., N | Λ | Λ | Λ | Λ | Concn., N | Λ | Λ | Λ | Λ |
| 0·1 | 87·09 | 74·16 | 64·11 | 56·47 | 0·012 | 96·97 | 83·24 | — | 68·62 |
| 0·08 | 87·39 | 75·66 | 65·23 | 57·90 | 0·01 | 97·11 | 84·48 | 77·14 | 68·89 |
| 0·04 | 91·05 | 78·01 | 69·30 | 62·04 | 0·008 | 97·89 | 85·00 | 77·92 | 70·00 |
| 0·02 | 95·20 | 81·97 | 72·72 | 66·08 | 0·004 | 99·01 | 85·99 | 79·43 | 72·87 |
| 0·016 | 95·50 | 81·63 | 77·04 | 67·17 | 0·0008 | 100·85 | 87·97 | 81·87 | 75·96 |

TABLE 3. *Dioxan–water media.*

| | 10% | 20% | 30% | | 10% | 20% | 30% |
|---|---|---|---|---|---|---|---|
| $10^6\kappa$, mho | 3·82 | 1·52 | 1·42 | $10^6\kappa$ mho | 3·82 | 1·52 | 1·42 |
| *D* | 69·69 | 60·79 | 51·9 | *D* | 69·69 | 60·79 | 51·9 |
| Concn., N | Λ | Λ | Λ | Concn., N | Λ | Λ | Λ |
| 0·09 | 107·08 | — | — | 0·009 | 116·11 | 100·67 | 82·23 |
| 0·07 | 109·07 | — | — | 0·007 | 117·10 | 101·43 | 83·01 |
| 0·06 | 108·82 | — | — | 0·006 | 118·46 | 102·53 | 83·47 |
| 0·05 | 110·85 | — | — | 0·004 | 117·03 | 103·14 | 83·78 |
| 0·04 | 111·14 | 90·81 | 75·42 | 0·002 | 120·27 | 107·57 | 84·45 |
| 0·02 | 112·91 | 96·52 | 79·12 | 0·001 | 121·0 | 109·95 | 86·71 |
| 0·01 | — | 99·95 | 81·92 | | | | |

TABLE 4.

| Solvent | $\Lambda_0$ | $10^3\eta$ | $\Lambda_0\eta$ | Solvent | $\Lambda_0$ | $10^3\eta$ | $\Lambda_0\eta$ |
|---|---|---|---|---|---|---|---|
| Water | 149·86 | 8·949 | 1·34 | Water | 149·86 | 8·949 | 1·34 |
| 10% $C_4H_8O_2$ | 122·40 | 10·9 | 1·33 | 10% PrⁱOH | 103·81 | 12·84 | 1·34 |
| 20% | 111·11 | 12·9 | 1·43 | 20% | 75·22 | 18·47 | 1·38 |
| 30% | 88·21 | 14·3 | 1·26 | 30% | 59·00 | 23·71 | 1·43 |
| 20% $COMe_2$ | 102·14 | 13·15 | 1·34 | 40% | 48·91 | 27·95 | 1·37 |
| 30% | 90·0 | 13·60 | 1·22 | | | | |
| 40% | 84·32 | 13·34 | 1·13 | | | | |
| 50% | 78·92 | 12·30 | 0·97 | | | | |

preferentially solvate water molecules (Shaw and Butler, *Proc. Roy. Soc.*, 1930, *A*, **129**, 519; Bockris and Egan, *Trans. Faraday Soc.*, 1948, **44**, 151).

Fig. 7 shows that there is less tendency for the dioxan–water curve than for the curve of the other two solvent media to pass through a minimum. Dioxan, owing to its low dipole moment and large molecular size, is less capable of entering the solvation sheaths of the ions, even at higher dioxan concentrations. This would account for the low solubility of potassium chloride in 40% dioxan. With acetone–water and *iso*propanol–water media, however, there is a tendency for inversion of the slopes over the range studied. This would suggest that, at higher concentrations of the non-aqueous solvent, both organic solvents enter the solvation sheath. Over the concentration range studied (as long as the non-aqueous additions are small) the dielectric-constant lowering is predominant,

suggesting that hydration is little disturbed. However, with more non-aqueous solvent present, the latter enters into the solvation sheath, owing to decrease of dielectric constant.

As the dielectric constant of water is changed by non-aqueous additions, it is, unfortunately, accompanied by specific changes in the nature of the solvent. A quantitative treatment of the specific solvent effects due to organic solvent additions depends on (i) a more complete knowledge of the dielectric constant decrement, especially in the vicinity of an ion, (ii) organic solvent–water interactions, especially hydrogen bonding, and (iii) the solvation of ions in mixed solvents, which may lead to a diminution of mobility due to the reduction of potential of a central ion by dipole interaction with the solvation sheath. It is of interest that dioxan raises the relaxation time of water by a large factor, but hydrogen ions equally well raise the time (Magat, *J. Chem. Phys.*, 1948, **49**, 93); it is, however, impossible to generalise for other non-aqueous solvents.

NORTHERN POLYTECHNIC, HOLLOWAY, LONDON, N.7. [*Received, March 9th*, 1953.]

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## 558. *Studies with Boron Trichloride and Organic Sulphides. Part I. The Preparation and Properties of Di-n-butyl Sulphide–Boron Trichloride.*

By M. F. LAPPERT.

Addition of boron trichloride (whether 1 mol. or an excess) to di-*n*-butyl sulphide (1 mol.) afforded a liquid molecular complex, which decomposed only very slowly at high temperature to give boron trichloride and di-*n*-butyl sulphide. There was apparently no tendency for C–S fission, by contrast to the ready C–O fission in ether–boron trichloride systems. On hydrolysis the complex gave di-*n*-butyl sulphide, hydrogen chloride, and boric acid, whereas pyridine displaced di-*n*-butyl sulphide and gave pyridine–boron trichloride. *n*-Butanol (1 mol.) and the sulphide complex (1 mol.) gave a tri-*n*-butylsulphonium complex, $Bu^n_3SBCl_4$, (0·5 mol.) as a solid, the formula of which was shown by its reaction with pyridine and by hydrolysis whereupon tri-*n*-butylsulphonium chloride was obtained, and this with boron trichloride produced again the sulphonium–boron complex. The latter was also instantly formed by the action of tri-*n*-butylsulphonium chloride on di-*n*-butyl sulphide–boron trichloride, whereas the addition of diethyl ether to the sulphide complex afforded di-*n*-butyl sulphide, triethyl borate, and a di-*n*-butylethylsulphonium complex, $Bu^n_2EtSBCl_4$.

A WELL-KNOWN property of dialkyl sulphides is their ability to form addition compounds. For example, several complexes of di-*n*-butyl sulphide with platinous salts have been recorded by Löndahl (*J. pr. Chem.*, 1888, **38**, 512). Phillips, Hunter, and Sutton (*J.*, 1945, 146) have described a complex, di*iso*butyl sulphide–boron trichloride, prepared by the interaction of excess of the trichloride with the sulphide in ligroin. The compound could not be isolated in a pure state and was described as thermally unstable, but a pure specimen of a corresponding diethyl sulphide complex was obtained and was required for physicochemical measurements.

The addition of di-*n*-butyl sulphide (1 mol.) to boron trichloride (whether 1 or 2 mols.) gave at once a quantitative yield of a molecular complex, $Bu^n_2S,BCl_3$. This was a colourless viscous liquid which was not decomposed to any considerable extent when heated at 215° for 32 hr., 75% of the complex being recovered on distillation. There was no indication of *n*-butyl chloride having been formed, but some di-*n*-butyl sulphide and boron trichloride were obtained. Pyridine hydrochloride had no catalytic effect on the reaction.

The complex was readily hydrolysed, and addition of pyridine (1 mol.) at low temperature to the complex (1 mol.) gave a high yield of pyridine–boron trichloride, which has previously been prepared by Gerrard and Lappert (*J.*, 1951, 1020; *Chem. and Ind.*, 1952, 53) and di-*n*-butyl sulphide.

$$Bu^n_2S,BCl_3 + 3H_2O \longrightarrow Bu^n_2S + H_3BO_3 + 3HCl$$
$$Bu^n_2S,BCl_3 + C_5H_5N \longrightarrow C_5H_5N,BCl_3 + Bu^n_2S$$

It is of interest to compare the reactivity of the two boron trichloride complexes towards hydrolysis and alcoholysis. While these reactions are now shown to go to completion at 20° for the di-*n*-butyl sulphide complex, this is not so with the pyridine complex, for which several hours' heating is required (Lappert, *J.*, 1953, 667).

The addition of *n*-butyl alcohol (1 mol.) to di-*n*-butyl sulphide–boron trichloride (1 mol.) afforded hydrogen chloride (1 mol.) at 20°. Crystallisation commenced after some days and was complete after about 3 weeks. The crystals were those of a new co-ordination compound, $Bu^n_3S,BCl_4$, the other products being tri-*n*-butyl borate, tri-*n*-butyl sulphide, and boron trioxide :

$$2Bu^n_2S,BCl_3 + 2Bu^nOH \longrightarrow Bu^n_3S,BCl_4 + 2HCl + Bu^nO\cdot BO$$
$$3Bu^nO\cdot BO \longrightarrow (Bu^nO)_3B + B_2O_3$$

The addition of *n*-butyl alcohol (2 or 3 mols.) to di-*n*-butyl sulphide–boron trichloride (1 mol.) was less complex and proceeded as follows (at 20°) :

$$2Bu^nOH + Bu^n_2S,BCl_3 \longrightarrow 2HCl + Bu^n_2S + (Bu^nO)_2BCl$$

Further decomposition to trialkyl borate followed, and then the reaction :

$$3Bu^nOH + Bu^n_2S,BCl_3 \longrightarrow 3HCl + Bu^n_2S + (Bu^nO)_3B$$

The evidence for considering the tri-*n*-butylsulphonium complex to have the formula $Bu^n_3S,BCl_4$ is summarised in the reactions illustrated below. However, two alternative structural possibilities, $[Bu^n_3S]^+[BCl_4]^-$ and $[Bu^n_3S,BCl_3]^+Cl^-$, cannot be distinguished by these experiments although the former is considered the more probable.

$$Bu^nCl + Bu^n_2S,BCl_3 \xleftarrow{\text{Heat}} Bu^n_3S,BCl_4 \xrightarrow[\text{b.p.}]{C_5H_5N} C_5H_5N,BCl_3 + Bu^n_2S \quad (+ \text{BuCl, not isolated})$$

$$Bu^nCl + Bu^n_2S \xleftarrow{\text{Heat}} [Bu^n_3S]^+Cl^- \xrightarrow{BCl_3} [Bu^n_3S]^+Cl^- \xrightarrow{3H_2O} [Bu^n_3S]^+Cl^- + 3HCl + H_3BO_3$$

When shaken with cold water for some hours the sulphonium complex dissolved, and titration with sodium hydroxide revealed only 0·75 equivalent of chloride as hydrochloric acid, whereas all the boron was present as boric acid. When this solution was saturated with solid sodium hydroxide crude tri-*n*-butylsulphonium chloride separated as a yellow oil which was reconverted into its boron complex by addition of boron trichloride. On distillation tri-*n*-butylsulphonium chloride decomposed to *n*-butyl chloride and di-*n*-butyl sulphide, whereas heating of the sulphonium–boron complex gave *n*-butyl chloride and di-*n*-butyl sulphide–boron trichloride. The sulphonium–boron complex was soluble in cold pyridine but without reaction, but when the solution was boiled pyridine–boron trichloride and di-*n*-butyl sulphide were obtained. This may have been due to the decomposition of the sulphonium–boron complex by heat and subsequent reaction of pyridine with the di-*n*-butyl sulphide–boron trichloride thus formed. Tri-*n*-butylsulphonium chloride quickly displaced the di-*n*-butyl sulphide from its boron trichloride complex.

*Fission of* C–S *and* C–O *Bonds in Ethers and Sulphides.*—Gerrard and Lappert (*J.*, 1952, 1486) have shown that the C–O bond in aliphatic ethers was broken with great ease (*e.g.*, at −80°) by reaction with boron trichloride ($ROR' + BCl_3 \longrightarrow RCl + R'O\cdot BCl_2$) and that the reaction appeared to be of $S_N1$ type. Other examples of ether fission are well established. Resistance to fission of a C–S bond in dialkyl sulphides by a variety of reagents is, however, considerable (Tarbell and Harnish, *Chem. Reviews*, 1951, **49**, 1). In the present experiments C–S fission did not occur.

The following mechanism of ether fission by boron trichloride was suggested :

$$R-\ddot{O}-R' + BCl_3 \longrightarrow \underset{\substack{| \\ {}^-BCl_3 \\ \text{(I)}}}{R\cdot\overset{+}{O}\cdot R'} \longrightarrow \underset{\text{(II)}}{R^+[R'O\cdot BCl_3]^-} \longrightarrow R^+ + Cl^- + R'O\cdot BCl_2 \longrightarrow RCl + RO\cdot BCl_2$$

The difference between the S and the O systems appears to be in stage (I). Whereas the di-*n*-butyl sulphide–boron trichloride probably has a structure analogous to (I), the ether complex has only transient existence and very rapidly rearranges to (II). This view is taken in the light of the work of Greenwood, Martin, and Emeléus (*J.*, 1950, 3030) with the boron trifluoride–diethyl ether complex, the structure of which was shown to be $Et^+[EtO{\cdot}BF_3]^-$.

## Experimental

*Interaction of Di-*n*-Butyl Sulphide and Boron Trichloride.*—(*a*) Di-*n*-butyl sulphide (4·19 g., 1 mol.) was added during 30 min. to boron trichloride (3·38 g., 1 mol.) at −80°. A yellow, viscous liquid was obtained which fumed (hydrogen chloride) only slightly in air. The mixture was kept at 20°/20 mm. for 30 min., but no condensate appeared in a trap at −80°. Distillation of 7·52 g. afforded crude *di-*n*-butyl sulphide–boron trichloride* (6·40 g., 85%), b. p. 78—85°/0·5 mm. (Found: Cl, 38·3; B, 3·9. $C_8H_{18}SBCl_3$ requires Cl, 40·4; B, 4·1%), which, purified by redistillation, had b. p. 83°/0·5 mm., $n_D^{21}$ 1·4960 (Found: Cl, 39·8; B, 4·0%). From the first distillation, a dark residue (0·46 g.) remained and di-*n*-butyl sulphide (0·34 g.), $n_D^{20}$ 1·4534, was collected in the trap at −80°.

(*b*) Di-*n*-butyl sulphide (4·21 g., 1 mol.) was added during 35 min. to boron trichloride (6·70 g., 2 mols.) at −80° (final wt. 10·82 g.), but copious fuming, due to boron trichloride, was evident. The whole was left at −10°/20 mm. for 15 min. (loss in wt., 3·30 g. Calc.: loss in weight due to 1 mol. of boron trichloride, 3·35 g.) and then afforded di-*n*-butyl sulphide–boron trichloride, b. p. 88—94°/0·4 mm. (6·5 g., 86%), and a residue (0·45 g.). The complex, when redistilled, had b. p. 80°/0·4 mm., $n_D^{20}$ 1·4953, $d_4^{17\cdot5}$ 1·145 (Found: Cl, 39·9; B, 4·05%).

The di-*n*-butyl sulphide–boron trichloride complex did not crystallise, even at 0° during several weeks.

*Hydrolysis of Di-*n*-Butyl Sulphide–Boron Trichloride.*—The complex (1·50 g.) was shaken with water (20 c.c.), then extracted with ether. The ethereal solution was washed with aqueous sodium carbonate and water, and dried ($MgSO_4$). On evaporation and distillation, di-*n*-butyl sulphide (0·75 g., 91%), b. p. 74°/10 mm., $n_D^{21}$ 1·4532, was obtained.

A sample (0·2904 g.) was hydrolysed in an enclosed system (to avoid escape of hydrogen chloride evolved). Direct titration with carbonate-free 0·0765N-sodium hydroxide (methyl-red) required 42·6 c.c. On addition of phenolphthalein and mannitol a further 14 c.c. of the hydroxide solution were required for neutralisation. The two titrations thus represent respectively 0·119 g. of HCl (checked by a Volhard estimation) and 0·068 g. of $H_3BO_3$ (corresponding to Cl, 39·9; B, 4·1%).

*Effect of Heat on Di-*n*-Butyl Sulphide–Boron Trichloride.*—The complex (4·88 g.) was heated at 215° for 32 hr. under a condenser attached to a potassium hydroxide absorption tube. Some darkening was observed and boron trichloride (0·45 g., 21%) was trapped (Found: Cl, 0·408 g.; B, 0·0413 g.). The remainder (4·41 g.) had a black sediment and afforded on distillation unchanged di-*n*-butyl sulphide–boron trichloride (3·71 g., 76%), b. p. 78—84°/0·4 mm., $n_D^{25}$ 1·4914 (Found: Cl, 38·0; B, 3·8%), di-*n*-butyl sulphide (collected at −80°) (0·43 g., 16%), $n_D^{25}$ 1·4510, and a black residue (0·23 g.).

Di-*n*-butyl sulphide–boron trichloride (5·34 g.) was heated at 100° for 24 hr. in the presence of anhydrous pyridine hydrochloride (0·154 g.) under the same conditions as above. After evacuation (20 mm.) the residue (5·43 g.) was distilled, affording the unchanged complex (4·8 g.), b. p. 88°/0·5 mm., $n_D^{20}$ 1·4950 (Found: Cl, 38·2; B, 4·0%).

*Interaction of Pyridine (1 Mol.) and Di-*n*-Butyl Sulphide–Boron Trichloride (1 Mol.).*—Pyridine (0·61 g., 1 mol.) in *n*-pentane (5 c.c.) was added to the complex (2·00 g., 1 mol.) at −10°. The addition was vigorous and a white precipitate was formed instantly. The mixture was set aside for 15 min. and the precipitated pyridine–boron trichloride (1·354 g., 91%), m. p. 114° (Found: Cl, 53·8. Calc. for $C_5H_5NCl_3B$: Cl, 54·2%), was filtered off. The filtrate, after removal of the solvent under vacuum, yielded di-*n*-butyl sulphide (0·96 g., 87%), b. p. 74°/14 mm., $n_D^{20}$ 1·4536.

*Addition of* n*-Butyl Alcohol (1, 2, and 3 Mols. severally) to the Complex (1 Mol.).*—*n*-Butyl alcohol (1·10 g., 1 mol.) was added to di-*n*-butyl sulphide–boron trichloride (3·90 g., 1 mol.) at 15°. The reaction was vigorous and hydrogen chloride was instantly evolved and absorbed by potassium hydroxide. The mixture was left for 15 hr. at 15°, whereafter analysis of the contents of the absorption tube showed that hydrogen chloride (0·531 g., 98%) had evolved. Next day crystallisation had begun and 21 days were allowed for its completion. Pentane was then added and the mixture filtered, yielding solid *tri-*n*-butylsulphonium chloride–*

*boron trichloride* (1·98 g.) (Found: C, 40·3; H, 7·6; S, 8·9; Cl, 40·3; B, 3·1. $C_{12}H_{27}SCl_4B$ requires C, 40·5; H, 7·7; S, 9·0; Cl, 39·9; B, 3·05%). The filtrate, after evaporation, fumed slightly (Found: Cl, 3·3; B, 5·5%) and afforded di-*n*-butyl sulphide (1·2 g.) contaminated with a little tri-*n*-butyl borate (b. p. 68—70°/10 mm., $n_D^{19}$ 1·4500) (Found: B, 0·85%), tri-*n*-butyl borate (0·43 g.), b. p. 68°/0·2 mm., $n_D^{19}$ 1·4200 (Found: B, 4·6. Calc. for $C_{12}H_{27}O_3B$: B, 4·7%), and a residue (0·62 g.), smelling of butyl alcohol and containing boron.

In a second experiment *n*-butyl alcohol (4·74 g., 1 mol.) was added to the di-*n*-butyl sulphide complex (17·3 g., 1 mol.). The mixture was set aside for 8 weeks, whereafter tri-*n*-butylsulphonium chloride–boron trichloride (11·70 g., 100%) (Found: Cl, 39·9; B, 3·0%) was filtered off. The filtrate, on fractionation, afforded di-*n*-butyl sulphide (4·32 g., 90%), b. p. 82—86°/22 mm., $n_D^{20}$ 1·4532, tri-*n*-butyl borate (1·82 g., 72%), b. p. 120—124°/24 mm. (redistilled: b. p. 117°/15 mm., $n_D^{20}$ 1·4112. Found: B, 4·8%), and a residue of boron trioxide (0·72 g., 94%). Yields in this experiment are calculated on the reaction: $2Bu^n{}_2S,BCl_3 + 2Bu^nOH \longrightarrow 2HCl + Bu^n{}_3SCl,BCl_3 + Bu^nO{\cdot}BO$; $3Bu^nO{\cdot}BO \longrightarrow B_2O_3 + (RO)_3B$.

*n*-Butyl alcohol (2·94 g., 2 mols.) was added to di-*n*-butyl sulphide–boron trichloride (5·23 g., 1 mol.) at 15°. After 14 days there was no crystallisation; the absorption tubes had trapped hydrogen chloride (1·46 g., 100%). The residue (6·72 g.) was heated at 80°/0·5 mm. and a condensate (6·2 g.) (Found: Cl, 8·0; B, 3·0%) was collected at −80°. There remained what appeared to be a mixture (0·38 g.) of the complex and boron trioxide (Found: Cl, 7·6; B, 6·9%). The condensate was difficult to fractionate; the first portion (4·55 g.), b. p. 72—100°/12 mm., $n_D^{15}$ 1·4398 (Found: Cl, 4·6; B, 2·3%), was probably a mixture of di-*n*-butyl sulphide (49%), tri-*n*-butyl borate (42%), and the complex (9·0%); the second was pure tri-*n*-butyl borate (1·1 g.), b. p. 104—106°/10 mm., $n_D^{15}$ 1·4168 (Found: B, 4·7%); a distillation residue (0·23 g.) remained.

*n*-Butyl alcohol (2·22 g., 3 mols.) was added to di-*n*-butyl sulphide–boron trichloride (2·62 g., 1 mol.) at 15°. After 20 hr., the absorption tubes had trapped hydrogen chloride (1·06 g., 98%). Quantitative fractionation, again difficult, gave fractions: I (1·30 g.), b. p. 68—72°/10 mm., $n_D^{20}$ 1·4538 (Found: B, 0·3%); II (1·12 g.), b. p. 72—101°/10 mm., $n_D^{20}$ 1·4200 (Found: B, 4·0%); and III (1·24 g.), b. p. 104—106°/10 mm., $n_D^{20}$ 1·4133 (Found: B, 4·6%). Fractions I and III were apparently fairly good specimens of di-*n*-butyl sulphide and tri-*n*-butyl borate respectively, and the middle fraction was a mixture with a large preponderance of the latter.

*Hydrolysis of Tri-*n*-Butylsulphonium Chloride–Boron Trichloride.*—Water (20 c.c.) was added to the complex (0·1540 g.). There was no immediate reaction and in order to dissolve the crystals mechanical shaking for about 2 hr. was required. No oil (*n*-butyl chloride or di-*n*-butyl sulphide) was formed. Titration with carbonate-free 0·102N-sodium hydroxide required 12·6 c.c. (methyl-red), and a further 4·75 c.c. after addition of mannitol and phenolphthalein (*i.e.*, 0·0472 g. of HCl and 0·0271 g. of $H_3BO_3$. Calc.: $H_3BO_3$, 0·0268 g.; $\frac{3}{4}$Cl as HCl, 0·0475 g.). Nitric acid and standard silver nitrate solution were added and chlorine ion was estimated by the Volhard method (Found: Cl, 40·1%).

The complex (4·00 g.) gave a clear solution in warm 3N-sodium hydroxide (10 c.c.), and this was saturated with solid sodium hydroxide, a light brown oil separating as upper layer. This was insoluble in ether and *n*-pentane, but was soluble in methylene dichloride. The solvent layer was dried ($K_2CO_3$) and the solvent removed at 0·01 mm. A viscous oil, crude *tri-*n*-butylsulphonium chloride* (2·54 g., 95%) [Found: Cl (Volhard, cold), 12·9. $C_{12}H_{27}SCl$ requires Cl, 14·9%], $n_D^{20}$ 1·5036, not volatile at 25°/0·005 mm., remained. The % yield is based on the reaction: $Bu^n{}_2S,BCl_3,Bu^nCl + 3H_2O \longrightarrow Bu^n{}_2S,Bu^nCl + 3HCl + H_3BO_3$.

*Effect of Heat on Tri-*n*-Butylsulphonium Chloride–Boron Trichloride.*—The complex (2·87 g.) was heated at 180°/0·3 mm. for 2 hr. A yellow liquid (di-*n*-butyl sulphide–boron trichloride) (1·78 g., 84%) (redistilled: b. p. 83—84°/0·5 mm., $n_D^{20}$ 1·4975. Found: Cl, 40·3; B, 4·07%) gradually distilled, leaving a carbonaceous residue (0·20 g.). In a trap at −80° a clear liquid (0·88 g.) was collected which on distillation afforded *n*-butyl chloride (0·66 g., 89%), b. p. 77—79°, $n_D^{17}$ 1·4051, $d_4^{26}$ 0·885 [Found: Cl (sealed tube), 38·1. Calc. for $C_4H_9Cl$: Cl, 38·4%], and a residue (0·19 g.) of di-*n*-butyl sulphide, $n_D^{20}$ 1·4520. Yields are based on the reaction: $Bu^n{}_2S,BCl_3,Bu^nCl \longrightarrow Bu^n{}_2S,BCl_3 + Bu^nCl$).

*Interaction of Pyridine and Tri-*n*-Butylsulphonium Chloride–Boron Trichloride.*—Pyridine (0·50 g.) was poured on tri-*n*-butylsulphonium chloride–boron trichloride (0·520 g.) at 20°. The solid dissolved and the solution was set aside at 20° for 2 hr., then placed in a vacuum (0·01 mm.). A crystalline residue (0·524 g.) of unchanged complex (Found: Total Cl, 39·4; B, 3·1%) remained.

To the complex (2·35 g.), pyridine (4·00 g.) was added and the solution was heated at 90° under reflux for 2 hr., a slight flocculent precipitate being formed. The mixture was cooled and placed at 25 mm., but no volatile matter was removed (*i.e.*, no free *n*-butyl chloride). The precipitate (0·036 g.) was filtered off and washed with pyridine (3 g.). The filtrate was then evacuated (0·2 mm.). Solid pyridine–boron trichloride (1·30 g., 100%) remained. The condensate collected in a trap at −80° was washed with dilute hydrochloric acid (to remove pyridine) and extracted with ether, and the ethereal layer was dried ($K_2CO_3$). After removal of the solvent, di-*n*-butyl sulphide (0·94 g., 97%), b. p. 71—80°/17 mm., $n_D^{24}$ 1·4518, was distilled. The pyridine–boron trichloride residue from the primary distillation, recrystallised from chloroform–*n*-pentane, had m. p. 114° (Found: Cl, 53·7; $C_5H_5N$, 40·2. Calc. for $C_5H_5N,Cl_3B$: Cl, 54·2; $C_5H_5N$, 40·3%). % Yields are based on the reaction: $Bu^n{}_3SCl,BCl_3 + C_5H_5N \longrightarrow C_5H_5NBCl_3 + Bu^n{}_2S + Bu^nCl$.

*Effect of Heat on Tri-*n*-Butylsulphonium Chloride.*—Distillation of tri-*n*-butylsulphonium chloride (2·00 g.) was attempted at 20 mm. At 100°, decomposition took place, di-*n*-butyl sulphide (0·96 g., 79%), b. p. 72—75°/17 mm., $n_D^{21}$ 1·4507, distilled, and a dark residue (0·15 g.) remained. In a trap at −80° *n*-butyl chloride (0·62 g., 80%), $n_D^{20}$ 1·4030, was collected; distilled, it had b. p. 75—79°, $n_D^{21}$ 1·4000 [Found: Cl (sealed tube), 38·0%]. % Yields are based on the reaction: $Bu^n{}_3SCl \longrightarrow Bu^n{}_2S + Bu^nCl$).

*Interaction of Boron Trichloride (1 Mol.) and Tri-*n*-Butylsulphonium Chloride (1 Mol.).*—Tri-*n*-butylsulphonium chloride (2·97 g., 1 mol.) in methylene dichloride (10 c.c.) was added to boron trichloride (2·90 g., >1 mol.) at −80°, and the mixture was left for 10 hr. at 20°, then placed in a vacuum, initially by using a water-pump and finally at 0·01 mm. A solid residue, tri-*n*-butylsulphonium chloride–boron trichloride (4·48 g., 100%) [Found: Cl (methyl-red), 29·5, (Volhard), 39·4; B, 3·1%] remained.

*Interaction of Diethyl Ether and Di-*n*-Butyl Sulphide–Boron Trichloride.*—Diethyl ether (1·78 g., >1 mol.) was added to di-*n*-butyl sulphide (4·19 g., 1 mol.) at −80°. After 12 hr. at 20°, distillation afforded di-*n*-butyl sulphide (1·11 g., 96%), b. p. 60°/9 mm., $n_D^{20}$ 1·4529, and triethyl borate (1·13 g., 98%) was collected at −80°, (b. p. 115—117°/760 mm., $n_D^{20}$ 1·3737) (Found: B, 7·5. Calc. for $C_6H_{15}O_3B$: B, 7·4%). The residual liquid (2·64 g., 100%) was non-volatile, even at 180°/0·1 mm., was water-soluble, and appeared to be *di-*n*-butylethylsulphonium chloride–boron trichloride* [Found: Cl (methyl-red titration), 31·5; Total Cl, 42·6; B, 3·24. $C_{10}H_{23}Cl_4SB$ requires $\frac{3}{4}$Cl, 32·3; Total Cl, 43·4; B, 3·30%]. The % yields are based on the reaction: $2Bu^n{}_2S,BCl_3 + 3(Et)_2O \longrightarrow Bu^n{}_2S + (EtO)_3B + EtBu^n{}_2SCl,BCl_3 + 2EtCl$ (not isolated).

*Interaction of Tri-*n*-Butylsulphonium Chloride and Pyridine–Boron Trichloride.*—Pyridine–boron trichloride (1·51 g., 1 mol.) in methylene dichloride (4 c.c.) was added to tri-*n*-butylsulphonium chloride (1·84 g., 1 mol.), and the mixture kept at 20° for 12 hr., then the solvent was removed. Water was added and the solid pyridine–boron trichloride, m. p. 114° (1·39 g., 92%), was recovered. Water was removed from the filtrate by evacuation over concentrated sulphuric acid, and tri-*n*-butylsulphonium chloride (1·63 g., 89%) was recovered as a viscous oil.

*Addition of Tri-*n*-Butylsulphonium Chloride (1 Mol.) to Di-*n*-Butyl Sulphide–Boron Trichloride (1 Mol.).*—Di-*n*-butyl sulphide–boron trichloride (1·65 g., 1 mol.) was added to tri-*n*-butylsulphonium chloride (1·49 g., 1 mol.) at 15°. There was instantaneous formation of solid and, after addition of pentane, tri-*n*-butylsulphonium chloride–boron trichloride (2·10 g., 91%) [Found: Cl, (methyl red) 29·5, (total) 39·5; B, 3·0%] was filtered off. The filtrate on distillation afforded di-*n*-butyl sulphide (0·90 g., 98%), b. p. 68—70°/12 mm., $n_D^{23}$ 1·4530.

The author is indebted to Dr. W. Gerrard for encouragement and helpful discussions and to Dr. L. Bateman, of the British Rubber Producers' Research Association, for his interest and for kindly supplying the di-*n*-butyl sulphide.

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## 559. *The Ultra-violet Absorption Spectra of Some Pyrroles.*

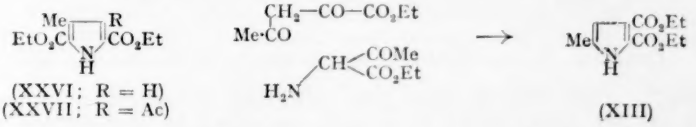
By Gerald H. Cookson.

The ultra-violet absorption spectra of a number of pyrroles have been measured and their dependence on the position of electron-attracting substituents is illustrated. Consideration of these results has led to the revision of the structures assigned to several compounds. The preparation of some pyrroles fused to a heterocyclic ring in the 2 : 3-positions is described.

The type of ultra-violet absorption spectrum shown by a pyrrole conjugated with a chromophore is dependent on the position of substitution. The striking contrast between the absorption curves given by pyrroles with an electron-attracting group in the 2- and 3-positions is shown in Fig. 1, and the curves for the various isomers with two such groups are given in Figs. 2 and 3. The spectra of individual examples are summarized in the Table, from which it appears that the general effects observed in the benzene series also apply here (Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414). Thus, substitution of a nuclear hydrogen by a methyl group shifts the bands 5—10 mμ towards the red, and replacement of a carbethoxyl by a formyl or acetyl group causes a bathochromic shift of *ca.* 20 mμ. A bromo-group has an effect similar to that of methyl.

Very few spectra of pyrroles have been published, and in a recent review (Granick and Gilder, *Adv. Enzymol.*, 1947, **7**, 358) the unjustified generalization, based on a single example (VII) (Pruckner and Dobeneck, *Z. physikal. Chem.*, 1942, **190**, *A*, 43), was made that "the spectrum of a substituted pyrrole consists of a single major band in the region 250—300 mμ."

The application of these results to a structural problem may be illustrated by reference to the condensation between ethyl α-aminoacetoacetate and ethyl acetopyruvate in acetic acid. Two pyrroles are formed, one of which was correctly identified as ethyl 5-carbethoxy-2 : 4-dimethyl-3-pyrrolylglyoxylate (XVIII) by Kordo, Ono, and Sato (*J. Pharm. Soc. Japan*, 1934, **54**, 123, 683). The other product, a (dicarbethoxy)methylpyrrole, m. p. 61°, was said to give no mixed m. p. depression with the ethyl ester of the ester acid, $C_9H_{11}O_4N$, m. p. 207°, which the Japanese chemists obtained when the condensation was carried out in aqueous sodium hydroxide. They obtained the same ester acid, m. p. 207°, by the use of glycine ester instead of ethyl α-aminoacetoacetate in the alkaline condensation, and both samples were decarboxylated to an ethyl methylpyrrolecarboxylate, m.p. 88°. They concluded that the substance, m. p. 61°, was diethyl 3-methylpyrrole-2 : 5-dicarboxylate (XXVI), and hence, by exclusion of the known 2 : 3-isomer, that the compound, m. p. 88°, was ethyl 4-methylpyrrole-2-carboxylate (*ibid.*, 1937, **57**, 1). These results appeared improbable. The Japanese assumed that (XXVI) was formed by hydrolysis of the nuclear acetyl group from the presumed intermediate (XXVII) in which in fact it is firmly attached (Lichtenwald, *Z. physiol. Chem.*, 1942, **273**, 118). Secondly, Fischer, Beyer, and Zaucker (*Annalen*, 1931, **486**, 55) have shown that the way in which acetylpyruvic ester condenses with an amino-ketone is dependent on pH; at pH < 6 the amino-group condenses exclusively with the acetyl group (leading here to XVIII) and only in strongly alkaline solution does it react with the oxalyl group (which would be required for the formation of XXVII).



(XXVI; R = H)
(XXVII; R = Ac)

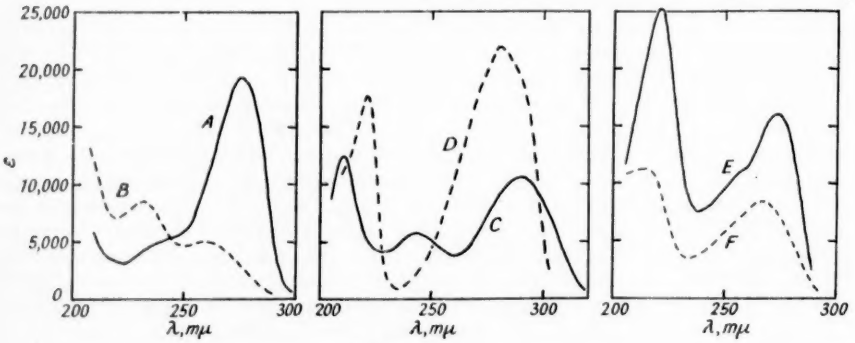
(XIII)

It is evident that the "extra" acetyl group which is lost during the formation of the compound, m. p. 61°, is removed by a reaction of the type discovered by Fischer and Fink (*Z. physiol. Chem.*, 1948, **283**, 152), and that in fact the product is (XIII). Had the amino-group condensed with the oxalyl CO, a similar reaction would have given (XXVI). This is unlikely since, if the amino-group had reacted in two ways, a mixture of all four pyrroles (XVIII), (XIII), (XXVI), and (XXVII) might have been expected, whereas only

(XVIII) and one other were obtained. The true structure (XIII) was proved by the close similarity of its absorption spectrum to that of diethyl 4 : 5-dimethylpyrrole-2 : 3-dicarboxylate (XIV), while the spectrum of a pyrrole with 2 : 5-dicarbethoxy-groups is entirely different. This was later confirmed by bromination of (XIII) to (XV), which was shown by m. p. and mixed m. p. to be different from diethyl 4-bromo-3-methylpyrrole-2 : 5-dicarboxylate (XIX). Although Corwin and Straughn (*J. Amer. Chem. Soc.*, 1948, **70**, 1416) quoted the Japanese results in support of their formulation, diethyl 3-methylpyrrole-2 : 5-dicarboxylate, which melts at 62°, the structure was proved by their own work. If the Japanese experimental data are accepted, it follows from the structure (XIII) by exclusion of the known 2 : 5-isomer that their compound, m. p. 88°, is actually ethyl 5-methylpyrrole-3-carboxylate. The condensations in alkaline solution have not been repeated.

Grob and Ankli (*Helv. Chim. Acta*, 1949, **32**, 2023), in their investigation of the products of the acetylation of 2 : 3-dihydro-2-oxopyrroles, explained the close similarity of the spectra of the compounds they called 2-acetoxy-3-acetyl-4-carbethoxypyrrole and its 5-methyl

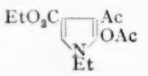
FIG. 1. FIG. 2. FIG. 3.



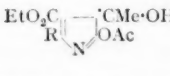

*Absorption spectra.*

FIG. 1. *A, Ethyl* 3 : 5-*dimethylpyrrole*-2-*carboxylate* (V). *B, Ethyl* 2 : 4-*dimethylpyrrole*-3-*carboxylate* (X).
FIG. 2. *C, Diethyl* 5-*methylpyrrole*-2 : 3-*dicarboxylate* (XIII). *D, Methyl* 5-*carbethoxy*-3-*ethyl*-4-*methyl pyrrole*-2-*carboxylate* (XX).
FIG. 3. *E, Diethyl* 3 : 5-*dimethylpyrrole*-2 : 4-*dicarboxylate* (XVI). *F, Diethyl* 2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate* (XXII).

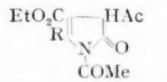
derivative, and their difference from that of 2-acetoxy-3-acetyl-4-carbethoxy-1-ethylpyrrole (XXVIII), by assuming that the first two compounds could tautomerise (XXIX). No evidence of such enolization has been found in the present work. The pyrrolylglyoxylate (XVIII), in which it would be most favoured, gives no colour with ferric chloride, and its ultra-violet spectrum is unaltered by alkali. Its infra-red spectrum in carbon tetrachloride, kindly measured by Dr. L. A. Duncanson, includes two bands at 3440




(XXVIII)




(XXIX; R = H or Me)




(XXX; R = H or Me)

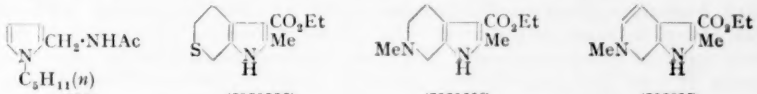
and 3300 cm.$^{-1}$. Their relative intensities vary with concentration in the manner expected for an NH group which is strongly associated in concentrated solutions; *i.e.*, on dilution the 3440 cm.$^{-1}$ band increases and that at 3300 cm.$^{-1}$ decreases in intensity. The spectrum of the solid shows only one NH frequency at 3220 cm.$^{-1}$. There is no sign of an OH frequency near 3500—3600 cm.$^{-1}$ throughout the concentration range studied (*ca.* 0·02—0·0036M). Both bands were present in the chloroform solution of (XVIII) at 3420 and 3290 cm.$^{-1}$, but the lower-frequency band was much weaker than its counterpart in similar concentration in carbon tetrachloride. The same pattern was found for the

spectrum of (XII) in chloroform (0·03M), the two frequencies in this case being 3450 and 3290 cm.$^{-1}$. From the changes with concentration observed in the intensities of the carbonyl bands of these compounds, it is concluded that the intermolecular association which takes place involves N–H···O bonds.

The compound (XXVIII) has an ultra-violet spectrum like that of (XXII) but with maxima shifted *ca.* 20 mμ towards the red, as expected, and its structure seems certain. The very close similarity of those of the other two compounds of Grob and Ankli, both with maxima at 315 mμ, contraindicates tautomerism. One would expect a pure enol (XXIX) with an azafulvene structure to absorb in the visible, so that a slight shift in the keto–enol equilibrium caused by the introduction of a methyl group would cause an appreciable difference between the spectra of the equilibrium mixtures of the two compounds. The compounds, unlike (XXVIII), are rapidly hydrolysed by cold sodium hydroxide to 3-acetyl-4-carbethoxy-2 : 3-dihydro-2-oxopyrroles and their spectra suggest that they still contain this system. They must therefore be the *N*-acetyl derivatives (XXX), the only other possibility (with both acetyl groups at position 3) being precluded by the blue colour produced by ferric chloride. Acetylation in position 1 is not unlikely, since 5-acetyl-4-carbethoxy-2 : 3-dihydro-2-oxopyrrole gives the *N*-methyl derivative with diazomethane.

Pyrrole itself absorbs weakly at 240 mμ (ε 300), in addition to the strong band at 210 mμ (ε 15,000) (in hexane; see Bowden, Braude, and Jones, *J.*, 1946, 948), but no sign of a low-intensity band in the 250-mμ region was observed in any of the alkylpyrroles studied (in alcohol). The absorption curves all fell smoothly with no inflexion, opsopyrrole (I) reaching ε 20 at 270 mμ, and (III) reaching ε 25 at 260 mμ. Low-intensity absorption is less significant in the case of cryptopyrrole (II) without special precautions being taken against its rapid atmospheric oxidation, but ε was less than 200 at 265 mμ.

The formation of a salt of cryptopyrrole was observed. The addition of a drop of hydrochloric acid to its alcoholic solution removed the band at 200 mμ and produced a new maximum at 261 mμ (ε 4000) (cf. *cyclo*pentadiene, 238·5 mμ; also Booker, Evans, and Gillam, *J.*, 1940, 1453). The acid solution was stable for at least 10 minutes, and the spectrum reverted to the neutral form on the addition of alkali, although measurements below 225 mμ could no longer be taken. Opsopyrrole (I), which has only two electron-donating alkyl groups, showed only a slight change in spectrum after the addition of much acid, whereas (III) and pyrroles with an electron-attracting group were unaffected.




(III) (XXIII) (XXIV) (XXV)

The preparation is described of the bicyclic pyrroles (XXIII—XXV). It had been hoped that useful intermediates for porphyrin syntheses could be obtained by opening the six-membered ring in such compounds.

## Experimental

Ultra-violet absorption spectra between ~210 and 400 mμ were measured in ethanolic solution with a Unicam spectrophotometer; 10-mm. cells were used except for (I) and (II), for which 1-mm. cells were used. The concentrations of the solutions employed were such that any maxima with $\varepsilon > 10\%$ of the most intense band recorded could be measured [except for (I) and (III) which were also examined at much higher concentrations; see above].

Compound (III) was kindly provided by Dr. Niels Elming (Elming and Clauson-Kaas, *Acta Chem. Scand.*, 1952, **6**, 867). Compound (VII) was prepared by hydrogenation of (XVII) in acetic acid containing 1% of concentrated hydrochloric acid over Adams's catalyst at 1 atm. It melted at 89—90° as reported by Signaigo and Adkins (*J. Amer. Chem. Soc.*, 1936, **58**, 709) and not at 96° (Siedel, *Z. physiol. Chem.*, 1935, **231**, 184). Pyrroles with only a 3-carbethoxy-group are hydrogenated to pyrrolines under these conditions. *Methyl 5-carbethoxy-3-ethyl-4-methylpyrrole-2-carboxylate* (XX), prepared from the ester acid with diazomethane, had m. p. 64—65° (Found: C, 60·4; H, 7·2; N, 6·1. $C_{12}H_{17}O_4N$ requires C, 60·2; H, 7·1; N, 5·9%). *4-Ethyl-3-methylpyrrole-2-carboxylic acid* (IV) was obtained by hydrolysis of its ester with

boiling N-sodium hydroxide in 50% ethanol for 45 min. and formed prisms, m. p. *ca.* 180—200° (effervescence) (Found : C, 62·5; H, 7·1; N, 9·2. $C_8H_{11}O_2N$ requires C, 62·7; H, 7·2; N, 9·15%). The aldehyde (XXI) melted at 92—93°, but the m. p. and preparation of the remaining compounds in the Table, apart from those described below, were in accordance with those in the literature (see Fischer and Orth, " Die Chemie des Pyrroles," Leipzig, 1934, Band I).

*Diethyl 5-Methylpyrrole-2 : 3-dicarboxylate* (XIII).—Zinc dust (8·4 g.) was added in portions to a stirred solution of ethyl hydroxyiminoacetoacetate (10·2 g.) and ethyl acetopyruvate (11·1 g.) in acetic acid (25 c.c.) with cooling to keep the temperature below 45°. The solution was then refluxed for 50 min., poured into water (300 c.c.) and extracted with benzene. After being washed with sodium hydroxide solution and with water, the extract was dried ($Na_2SO_4$), and the solvent removed. The residual oil (8·9 g.) was chromatographed on alumina in benzene, which eluted all the Ehrlich-positive reacting material (5 g.). This was again chromatographed on alumina in light petroleum (b. p. 40—60°)—ether (5 : 1). The first fractions yielded the *diester* (XIII), large colourless tablets [from light petroleum (b. p. 60—80°)], m. p. 62—63° (2·25 g., 15·6%) (Found : C, 58·8; H, 6·8; N, 6·2. $C_{11}H_{15}O_4N$ requires C, 58·65; H, 6·7; N, 6·2%). Later fractions from the chromatogram provided ethyl 5-carbethoxy-2 : 4-dimethyl-3-pyrrolylglyoxylate (XVIII) (0·6 g., 3·5%), m. p. 126—127·5° undepressed by admixture with a sample prepared by Fischer and Andersag's method (*Annalen*, 1927, **458**, 137). The 2 : 4-*dinitrophenylhydrazone* of (XVIII) separated in orange crystals (from ethyl acetate), m. p. 205—207° with slight previous softening (Found : C, 51·0; H, 5·0; N, 15·8. $C_{19}H_{21}O_8N_5$ requires C, 51·0; H, 4·7; N, 15·7%).

*Diethyl 4-Bromo-5-methylpyrrole-2 : 3-dicarboxylate* (XV).—A solution of diethyl 5-methylpyrrole-2 : 3-dicarboxylate (502 mg.) in boiling carbon tetrachloride (5 c.c.) was treated with bromine (1 mol.) in carbon tetrachloride. Hydrogen bromide was immediately evolved and after 1 min. suction was applied to remove the solvent. The *bromopyrrole* (XV), recrystallized twice from alcohol, formed prisms, m. p. 117·5—119° (146 mg., 22%) (Found : C, 43·55; H, 4·7; N, 4·65. $C_{11}H_{14}O_4NBr$ requires C, 43·4; H, 4·6; N, 4·6%). When mixed with its isomer (XIX), its m. p. was depressed to 70—79°.

3-*Hydroxyiminothia*cyclo*hexan-4-one*.—This was not isolated from solution. Attempts to prepare it from 3-carbomethoxythia*cyclo*hexanone with alkali and nitrite (cf. Geissman and Schlatter, *J. Org. Chem.*, 1946, **11**, 771) yielded only thia*cyclo*hexanone ; and reaction between the latter, sodium ethoxide, and ethyl nitrite (1 equiv.) in dry ether (cf. Pezold and Shriner, *J. Amer. Chem. Soc.*, 1932, **54**, 4707) gave a product heavily contaminated with 3 : 5-*bishydroxyiminothia*cyclo*hexan-4-one*, colourless efflorescent needles which charred on being heated (Found : C, 34·3; H, 3·3. $C_5H_6O_3N_2S$ requires C, 34·5; H, 3·45%).

Methyl 4-oxothia*cyclo*hexane-3-carboxylate (16·2 g.) was hydrolysed with potassium hydroxide (6·0 g. in 50 c.c. of water) at −10° for several weeks. Extraction of the solution with ether removed thia*cyclo*hexanone (3 g.), and further extraction with ether after careful acidification at −10° provided the free keto-acid (10 g.). This was dissolved in acetic acid (10 c.c.) and water (5 c.c.) and treated dropwise with concentrated aqueous sodium nitrite. Carbon dioxide was evolved, and the nitrite was rapidly consumed until 2·9 g. had been added. The yellow solution was kept at 0° for 3 hr. before use.

*Ethyl 4 : 5 : 6 : 7-Tetrahydro-2-methyl-1-aza-6-thiaindene-3-carboxylate* (XXIII).—Ethyl acetoacetate (6·5 g.) was added to the solution of the hydroxyimino-compound described above, and the mixture added in portions to zinc dust (6·5 g.) with mechanical stirring. The temperature was kept below 60° during the addition, after which the mixture was warmed for 30 min. and then poured on ice. The washed and dried precipitate gave a turbid solution in chloroform which was clarified by shaking it with alumina before pouring it through an alumina column. The material recovered from the eluate was further chromatographed in benzene on alumina. The *tetrahydroazathiaindene* (XXIII) (1·3 g., 6·5%) crystallized from ethanol or nitromethane in needles, m. p. 154·5—156°, which were sublimed at 165°/0·2 mm. before analysis (Found : C, 58·5; H, 6·6; N, 5·8. $C_{11}H_{15}O_2NS$ requires C, 58·6; H, 6·7; N, 6·2%). A solution of the compound in warm nitromethane containing methyl iodide soon deposited crystals of the *methiodide* (Found : C, 39·3; H, 5·2. $C_{12}H_{18}O_2NSI$ requires C, 39·2; H, 4·9%), which was converted into the *methopicrate*, golden needles (from ethanol), m. p. 134—137° (decomp.) (Found : C, 46·35; H, 4·3; N, 11·8. $C_{18}H_{20}O_9N_4S$ requires C, 46·2; H, 4·3; N, 12·0%).

3-Hydroxyimino-1-methyl-4-piperidone was not isolated from solution. Sodium hydroxide (10·75 g. in 20 c.c. of water) was added to a stirred solution of 3-carbethoxy-1-methyl-4-piperidone hydrochloride (25 g.) in water (50 c.c.) at 3°. The mixture was kept at this temperature with occasional shaking for 8—10 days. The temperature was then kept below 0° while first acetic

acid (72 c.c.) and then a solution of sodium nitrite (6·1 g. in 13 c.c. of water) were added. The addition of the nitrite (1 hr.) was accompanied by smooth evolution of carbon dioxide. The solution was set aside for 2 hr. before use.

*4′-Carbethoxy-1 : 2 : 5 : 6-tetrahydro-1 : 5′-dimethylpyrrolo(2′ : 3′-3 : 4)pyridine* (XXIV).—Ethyl acetoacetate (14·6 g.) was added to the solution of the foregoing hydroxyimino-compound, and the mixture gradually (45 min.) added to zinc dust (14·44 g.). The temperature rose to 50°. Stirring was continued while the mixture was refluxed for 4 hr. The product could be extracted with chloroform after the addition of enough 30% sodium hydroxide solution to the ice-cold reaction mixture to redissolve the zinc hydroxide. However, it was more convenient to remove the zinc first, by diluting the solution five times with water and saturating it with hydrogen sulphide. The supernatant liquid was made alkaline and extracted with chloroform. Evaporation of the solvent left a dark brown oil (9 g.) from which the pure product crystallized (2·1 g.). The *tetrahydropyrrolopyridine* (XXIV) separated from chloroform in colourless needles, which lost solvent of crystallization when warmed. The solvent-free base, which was very soluble in the common solvents, melted at 165—166° (Found: C, 65·2; H, 7·9; N, 13·0. $C_{12}H_{18}O_2N_2$ requires C, 64·9; H, 8·1; N, 12·6%). The *picrate* formed canary-yellow crystals (from ethanol), m. p. 180—186° (decomp.) (Found: C, 48·3; H, 4·7; N, 15·4. $C_{18}H_{21}O_9N_5$ requires C, 47·9; H, 4·7; N, 15·5%). A quantitative yield of the *methiodide* rapidly separated from a solution of the base in alcoholic methyl iodide and had m. p. 239—240° (decomp.) (Found: C, 43·0; H, 5·6; N, 7·65. $C_{13}H_{21}O_2N_2I$ requires C, 42·8; H, 5·8; N, 7·7%). The *methopicrate* crystallized from water in golden needles, m. p. 227—229° (Found: C, 48·25; H, 4·8; N, 15·4. $C_{19}H_{23}O_9N_5$ requires C, 49·0; H, 4·95; N, 15·05%).

*Hofmann degradation of methiodide of* (XXIV). Silver oxide could not be used since it gave a complex with the iodide which was soluble in methanol and deposited a silver mirror when heated. Sodium ethoxide (1 equiv.) was added to the methiodide (500 mg.) in ethanol (10 c.c.), and the solution refluxed for 2 hr. The *methine base* was obtained by removal of the solvent, addition of water, and extraction with benzene. After distillation at 130°/0·2 mm., it crystallized from light petroleum (b. p. 60—80°) in rhombs, m. p. 76—77° (Found: C, 62·9, 63·2; H, 9·1, 9·1; N, 9·6, 10·2%). Its *hydrochloride* separated in laths, m. p. 230—235° (effervescence),

*Absorption Characteristics of pyrrole derivatives*

| | R¹ | R² | R³ | R⁴ | $\lambda_{max.}$ | $\epsilon_{max.}$ | $\lambda_{min.}$ | $\epsilon_{min.}$ |
|---|---|---|---|---|---|---|---|---|
| (I) | H | Et | Me | H | ~203 | 5,670 | — | — |
| (II) | Me | Et | Me | H | ~200 | 7,450 | — | — |
| | | | | (+ HCl) | 261 | 4,000 | 231 | 2,000 |
| | | | | | Isosbestic point at | | 241 | 2,300 |
| (III) | | | (See text) | | 220 | 8,770 | — | — |
| (IV) | $CO_2H$ | Me | Et | H | 253 * | 9,700 | 220 | 2,660 |
| | | | | | 270 | 14,500 | — | — |
| (V) | $CO_2Et$ | Me | H | Me | 240 * | 5,000 | 221 | 3,000 |
| | | | | | 276 | 19,300 | — | — |
| (VI) | $CO_2Et$ | Me | $CH_2{\cdot}CH(CO_2Et)_2$ | Me | 247 * | 5,950 | 222·5 | 3,770 |
| | | | | | 280 | 19,200 | — | — |
| (VII) | $CO_2Et$ | Me | Et | Me | 250 * | 5,900 | 222 | 2,800 |
| | | | | | 283·5 | 18,900 | — | — |
| (VIII) | Ac | Me | Et | Me | 266 * | 4,700 | 235 | 800 |
| | | | | | 308 | 19,600 | — | — |
| (IX) | Me | Me | $CO_2Et$ | H | 231·5 | 9,980 | 220 | 7,960 |
| | | | | | 263·5 | 3,740 | 255 | 3,570 |
| (X) | Me | $CO_2Et$ | Me | H | 232 | 8,480 | 220 | 7,100 |
| | | | | | 259 | 5,030 | 250 | 4,670 |
| (XI) | Me | $CO_2Et$ | Me | Me | 232·5 | 9,400 | 222·5 | 8,760 |
| | | | | | 270 | 4,700 | 254 | 3,800 |
| (XII) | Me | Ac | Me | H | <210 | >10,000 | — | — |
| | | | | | 251 | 10,000 | 227 | 3,000 |
| | | | | | 273—285 * | 4,760 | — | — |
| (XIII) | $CO_2Et$ | $CO_2Et$ | H | Me | 210 | 12,400 | — | — |
| | | | | | 243 | 5,640 | 229 | 4,100 |
| | | | | | 290 | 10,570 | 260 | 3,670 |
| (XIV) | $CO_2Et$ | $CO_2Et$ | Me | Me | 213 | 8,000 | — | — |
| | | | | | 250 | 4,500 | 235 | 4,100 |
| | | | | | 293 | 10,500 | 263 | 3,900 |
| (XV) | $CO_2Et$ | $CO_2Et$ | Br | Me | <210 | >12,000 | 252 | 4,370 |
| | | | | | ε varies little between 230 and 255 mμ | | | |
| | | | | | 283 | 12,250 | — | — |

*Absorption Characteristics of pyrrole derivatives*

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $\lambda_{max.}$ | $\varepsilon_{max.}$ | $\lambda_{min.}$ | $\varepsilon_{min.}$ |
|---|---|---|---|---|---|---|---|---|
| (XVI) | $CO_2Et$ | Me | $CO_2Et$ | Me | 221 | 25,300 | 238 | 7,550 |
| | | | | | 273 | 16,100 | — | — |
| (XVII) | $CO_2Et$ | Me | Ac | Me | 235 | 22,800 | — | — |
| | | | | | 255 * | 12,000 | 268 | 8,800 |
| | | | | | 283 | 11,800 | — | — |
| (XVIII) | $CO_2Et$ | Me | $CO{\cdot}CO_2Et$ | Me | 243·5 | 25,200 | <210 | <6,000 |
| | | | | | 292 | 8,540 | 275 | 6,670 |
| (XIX) | $CO_2Et$ | Br | Me | $CO_2Et$ | 220 | 17,350 | 239 | 3,800 |
| | | | | | 278 | 20,250 | | |
| (XX) | $CO_2Et$ | Me | Et | $CO_2Me$ | 221 | 17,700 | 235 | 900 |
| | | | | | 280 | 21,900 | | |
| (XXI) | $CO_2Et$ | Me | Et | CHO | 231 | 14,200 | 215 | 6,500 |
| | | | | | 303 | 21,100 | 250 | 1,600 |
| (XXII) | Me | $CO_2Et$ | $CO_2Et$ | Me | 215 | 11,200 | 234 | 3,500 |
| | | | | | 267·5 | 8,450 | — | — |
| (XXIII) | (See text) | | | | ~212 | 14,600 | 252 | 3,700 |
| | | | | | 266 | 4,550 | — | — |
| | (Methiodide) | | | | <230 | high | 250 | 4,800 |
| | | | | | 262·5 | 5,500 | — | — |
| (XXIV) | (See text) | | | | ~208 | 17,500 | — | — |
| | | | | | 228 * | 9,150 | 250 | 3,820 |
| | | | | | 266·5 | 4,880 | — | — |
| | (in 0·05N-HCl in EtOH) | | | | ~208 | 17,500 | — | — |
| | | | | | 225 * | 9,000 | 244 | 4,800 |
| | | | | | 256 | 5,470 | — | — |
| | | | | | Isosbestic points at | | 241·5 | 4,800 |
| | | | | | | | and 263·5 | 4,800 |
| (XXV) | (See text) | | | | ~210 | 13,200 | — | — |
| | | | | | 227 | 11,600 | 218 | 11,400 |
| | | | | | 243 * | 9,700 | 280 | 1,000 |
| | | | | | 373·5 | 22,000 | — | — |
| | | | | (+HCl) | 212 | 15,000 | 229 | 7,770 |
| | | | | | 241 | 9,720 | 276 | 700 |
| | | | | | 348·5 | 20,800 | — | — |
| | | | | | Isosbestic points at | | ~220 | — |
| | | | | | | | ~280 | — |
| | | | | | | | and at 242 | 9,700 |
| | | | | | | | 359 | 17,000 |
| | Me | $CO_2Et$ | $>C_6H_4$ | | 215 | 35,500 | — | — |
| (3-Carbethoxy-2-methylindole) | | | | | 228 * | 18,000 | 243 | 9,150 |
| | | | | | 253 | 10,100 | 265 | 8,600 |
| | | | | | 282 | 11,300 | — | — |

* = Shoulder. $\lambda$ in m$\mu$.

from aqueous methanolic hydrochloric acid (Found: C, 55·9; H, 7·6; N, 9·7; Cl, 12·5%), and its *picrate*, m. p. 205—220° (decomp.), from alcohol (Found: C, 48·6; H, 4·9; N, 15·1%). These analyses are inconsistent with each other. The base had absorption maxima at 215 and 268 m$\mu$, which changed to 215 and 263·5 m$\mu$ with acid.

*4′-Carbethoxy-1 : 2-dihydro-1 : 5′-dimethylpyrrolo[2′ : 3′-3 : 4]pyridine* (XXV).—A solution of the tetrahydro-base (XXIV) (0·24 g.) in acetic acid (1·5 c.c.) and water (3 c.c.) was boiled with mercuric acetate (1·5 g.) for 20 min. The mercurous acetate was removed, and a solution of potassium bromide added to the filtrate. The supernatant liquid was decanted from the gum which was first precipitated and treated with more potassium bromide. The white needles of the *hydrogen mercuric tribromide salt* of (XXV) which then separated were recrystallized from water and had m. p. 168—169° (0·32 g.) (Found: C, 22·0; H, 2·6; N, 4·25. $C_{12}H_{17}O_2N_2Br_3Hg$ requires C, 21·8; H, 2·6; N, 4·2%). The *picrate* could be prepared from this complex salt or, better, by direct addition of picric acid to the reaction mixture. It crystallized from dioxan in yellow prisms, m. p. 201—206° (decomp.) (Found: C, 47·4; H, 4·3; N, 15·0. $C_{18}H_{19}O_9N_5,\frac{1}{2}H_2O$ requires C, 47·2; H, 4·4; N, 15·3%). The free *dihydro*-base (XXV) was regenerated from its picrate with lithium hydroxide and chromatographed on alumina in benzene, from which it was eluted by ethyl acetate containing 4% of methanol; crystallized from ethyl acetate, it formed very pale buff prisms, m. p. 140—149° (decomp.) (Found: C, 65·3; H, 7·1. $C_{12}H_{16}O_2N_2$ requires C, 65·45; H, 7·3%). It could not be sublimed. An earlier fraction from the chromatogram, eluted with benzene–ethyl acetate (1 : 1), provided a small amount of a colourless *substance*, m. p. 220—222°, which sublimed at its m. p. (Found: C, 61·5, 61·0; H, 7·05, 6·85; N, 11·3,

12·6. $C_{22}H_{30}O_5N_4$ requires C, 61·4; H, 7·0; N, 13·0%). Its spectrum, which was unchanged by acid, had maxima at 213, 263, and 276 mμ, $E^{1\%}_{1\,cm.}$ 1200, 515, and 540, respectively.

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## 560. *The Phthalates of* 3 : 5 : 5-*Trimethylhexan*-1-*ol.*

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Di-(3 : 5 : 5-trimethylhexyl) phthalate prepared from racemic 3 : 5 : 5-trimethylhexanol slowly deposits the racemic diester at 0°.

Racemic 3 : 5 : 5-trimethylhexanol has been optically resolved and the (++), (−−), racemic, and *meso*-forms of di-(3 : 5 : 5-trimethylhexyl) phthalate have been synthesised.

EVIDENCE has been presented (E. E. Turner and L. Turner, *J.*, 1951, 2543) that 3 : 5 : 5-trimethylhexan-1-ol, synthesised from a mixture of 2 : 4 : 4-trimethylpent-1- and -2-ene (di*iso*butylene), carbon monoxide, and hydrogen by the "oxo" reaction, is free from isomeric alcohols. The alcohol used in the present work was prepared by the "oxo" procedure and was fractionally distilled (b. p. 193·6°, reflux ratio 80 : 1) through a column of one hundred theoretical plates before use.

The work described below originated when a sample of di-(3 : 5 : 5-trimethylhexyl) phthalate prepared from phthalic anhydride and racemic 3 : 5 : 5-trimethylhexanol deposited a solid form of the diester. This, when purified (m. p. 26—29°), was thought to be either the racemic or the *meso*-dialkyl phthalate. E. E. Turner and L. Turner (*J.*, 1952, 1761) had already described the isolation of (+)-3 : 5 : 5-trimethylhexan-1-ol, by way of the brucine salt of racemic 3 : 5 : 5-trimethylhexyl hydrogen phthalate. This partial resolution has been completed (cf. Gilman and Blatt, "Organic Sytheses," Wiley, New York, Coll. Vol. I, 2nd Edn., p. 418). Hydrolysis of the (+)- and the (−)-hydrogen phthalate gave (+)- and (−)-3 : 5 : 5-trimethylhexan-1-ol respectively. On acid-catalysed esterification of (+)-3 : 5 : 5-trimethylhexyl hydrogen phthalate with (+)-3 : 5 : 5-trimethylhexanol, (++)-di-(3 : 5 : 5-trimethylhexyl) phthalate was obtained, and the (−−)-diester was prepared in the same way. Recrystallisation of an equimolar mixture of the (++)- and the (−−)-diester from methanol provided racemic di-(3 : 5 : 5-trimethylhexyl) phthalate (m. p. 26—29°), identical with the crystalline product isolated from the original mixture of racemic and *meso*-diesters.

Acid-catalysed esterification of (+)-3 : 5 : 5-trimethylhexyl hydrogen phthalate with (−)-3 : 5 : 5-trimethylhexanol would bring about ester exchange and give a mixture of racemic and *meso*-diesters. Therefore, *meso*-di-(3 : 5 : 5-trimethylhexyl) phthalate was synthesised by treating the silver salt of (+)-3 : 5 : 5-trimethylhexyl hydrogen phthalate with the iodide derived from (−)-3 : 5 : 5-trimethylhexanol. Unfortunately the *meso*-diester was obtained only as an oil. Since racemic di-(3 : 5 : 5-trimethylhexyl) phthalate remains unaffected by 2 hr.' heating at 200° it is unlikely that a thermal ester interchange has transformed the *meso*-di-(3 : 5 : 5-trimethylhexyl) phthalate into a mixture of racemic and *meso*-diester.

Haller (*Compt. rend.*, 1889, **108**, 410, 456) prepared (++)- and (−−)-dibornyl succinate and phthalate, in addition to the optically inactive mixture of racemic and *meso*-diesters given by the esterification of succinic or phthalic acid with racemic borneol. However, neither the *meso*-dibornyl succinate nor the corresponding phthalate was isolated. In a similar manner Quist (*Annalen*, 1918, **417**, 296) reported the synthesis of (++)-, (−−)-, and racemic difenchyl oxalates. Despite the extensive use of hydrogen phthalates for

resolution of alcohols (Hewitt and Kenyon, *J.*, 1925, 1094; Kenyon and Snellgrove, *ibid.*, p. 1169) no instance was known to the authors in which the four possible diesters of an asymmetric alcohol with a dibasic acid have been recorded.

## Experimental

Optical rotations were measured in a 4-dm. tube.

*Di*-(3 : 5 : 5-*trimethylhexyl*) *Phthalate*.—Phthalic anhydride (1 mol.), racemic 3 : 5 : 5-trimethylhexanol (4 mols.), and alumina (2% by wt. of the alcohol) were refluxed for 6 hr. in a glass apparatus, and the water (1 mol.) entrained in the refluxing alcohol was separated. The product was washed with dilute alkali, then water, and steam-distilled, to leave a viscous mixture of stereoisomeric *di*-(3 : 5 : 5-*trimethylhexyl*) *phthalates*, which were decanted from water and dried at 100° under reduced pressure (yield 90%) (Found : C, 74·3; H, 10·0; acid val., 0; sap. val., 264 mg. of KOH per g. $C_{26}H_{42}O_4$ requires C, 74·6; H, 10·1%; acid val. 0; sap. val. 268 mg.).

After being kept for some months at −5° the mixture of stereoisomers slowly began to crystallise. It was pressed on a porous plate at −10°, then allowed to warm to 20°, and the residual crystals were recrystallised five times from methanol and then three times from acetone to provide colourless needles of constant m. p. 26—29° (Found : C, 74·3; H, 9·9; acid val. 0; sap. val. 267 mg. of KOH per g.).

Hydrolysis of the crystalline phthalate gave phthalic acid, m. p. 195° (anhydride, m. p. 130°, imide, m. p. 233°) and racemic 3 : 5 : 5-trimethylhexan-1-ol. The latter was identified as the 3 : 5-dinitrobenzoate, lemon-yellow plates, m. p. 62° [from light petroleum (b. p. 40—60°)] undepressed on admixture with an authentic sample of the same m. p.

*Racemic* 3 : 5 : 5-*Trimethylhexyl Hydrogen Phthalate and its Resolution*.—Prepared following the method of E. E. Turner and L. Turner (*J.*, 1951, 2544), this ester had m. p. 52° (Found : C, 69·9; H, 8·1. Calc. for $C_{17}H_{24}O_4$ : C, 69·9; H, 8·2%).

A solution of it (70 g.) and anhydrous brucine (83·1 g.) in warm acetone (100 c.c.), on storage overnight, deposited rhombs (120·5 g.), m. p. 70—75°, which after crystallisation from acetone (250 c.c.) had m. p. 90—92° (74 g.). The first and the second acetone mother-liquors were combined. Two further recrystallisations of the brucine salt from acetone gave colourless prisms (60 g.) of unchanged m. p. and optical rotation. The (+)-3 : 5 : 5-trimethylhexyl hydrogen phthalate recovered from the brucine salt of m. p. 90—92° crystallised in colourless plates, m. p. 69° [from light petroleum (b. p. 40—60°)] (18·6 g.), $[\alpha]_D^{20}$ +7·0° ± 0·5° (*c* 4·0 in $CHCl_3$) (Found : C, 69·8; H, 8·2%).

Acetone was removed from the combined first and second mother-liquors, and the crude (−)-ester was retrieved. Three crystallisations from light petroleum (b. p. 40—60°) yielded (−)-3 : 5 : 5-trimethylhexyl hydrogen phthalate (15 g.), m. p. 69°, $[\alpha]_D^{20}$ −7·0° ± 0·5° (*c* 4·3 in $CHCl_3$) (Found : C, 70·1; H, 8·5%).

(+) *and* (−)-3 : 5 : 5-*Trimethylhexan*-1-*ol*.—Alkaline hydrolysis of the (+)- and the (−)-hydrogen phthalate gave (+)- and (−)-3 : 5 : 5-*trimethylhexan*-1-*ol*, respectively, b. p. 190—192°, $[\alpha]_D^{20}$ +4·5° ± 0·3° and −4·5° ± 0·3° (*c* 4·0 in $CHCl_3$) [Found : (+)-alcohol, C, 75·2; H, 13·7. (−)-alcohol, C, 74·8; H, 13·7. $C_9H_{20}O$ requires C, 75·0; H, 13·9%].

(+) *and* (−)-3 : 5 : 5-*Trimethylhexyl* 3 : 5-*dinitrobenzoate* were obtained as pale lemon-yellow needles, m. p. 56° [from light petroleum (b. p. 40—60°)], $[\alpha]_D^{20}$ +0·5° ± 0·3° and −0·5° ± 0·3° respectively (*c* 4·0 in $CHCl_3$) [Found : (+)-ester, C, 57·1; H, 6·6; N, 8·3. (−)-ester, C, 57·0; H, 6·6; N, 8·1. $C_{16}H_{22}O_6N_2$ requires C, 56·8; H, 6·5; N, 8·3%].

(++)-*Di*-(3 : 5 : 5-*Trimethylhexyl*) *Phthalate*.—(+)-3 : 5 : 5-trimethylhexan-1-ol (1·2 g.) and (+)-3 : 5 : 5-trimethylhexyl hydrogen phthalate (2 g.) in toluene (25 c.c.) were treated with concentrated sulphuric acid (1 drop). This mixture was refluxed for 4 hr. (Soxhlet), the toluene–water distillate being dried by magnesium sulphate in the thimble. After the toluene solution had been washed with dilute alkali, acid, and water, it was steam-distilled, and the residue was dried under reduced pressure at 100° and then sublimed (bath 180°/0·02 mm.). Two recrystallisations of the sublimate from the minimum of methanol gave colourless needles (2·0 g.) of (++)-*di*-(3 : 5 : 5-*trimethylhexyl*) *phthalate*, m. p. 37—38°, $[\alpha]_D^{20}$ +4·4° ± 0·3° (*c* 4·8 in $CHCl_3$), unchanged by further crystallisation (Found : C, 74·7; H, 10·2. $C_{26}H_{42}O_4$ requires C, 74·6; H, 10·1%).

(−−)-*Di*-(3 : 5 : 5-*trimethylhexyl*) *Phthalate*.—Prepared as outlined above for the (++)-isomer, this *ester* crystallised in colourless needles, m. p. 37—38°, $[\alpha]_D^{20}$ −4·4° ± 0·3° (*c* 4·7 in $CHCl_3$) (Found : C, 74·6; H, 10·2%).

*Racemic Di-(3 : 5 : 5-trimethylhexyl) Phthalate.* Equal quantities of (++)- and (−−)-di-(3 : 5 : 5-trimethylhexyl) phthalate were dissolved in, and crystallised from, the minimum of methanol at −60°, giving a colourless microcrystalline precipitate of racemic di-(3 : 5 : 5-trimethylhexyl) phthalate, m. p. and mixed m. p. 26—29°. It had m. p. 25—27° after 2 hr. at 200° under nitrogen.

(+)-3 : 5 : 5-*Trimethylhexyl Iodide [from (−)-Alcohol]*.—Red phosphorus (0·19 g.) and powdered iodine (2·13 g.) were added to (−)-3 : 5 : 5-trimethylhexanol (2 g.) at 0° and left overnight. This mixture was then warmed to 70° for 3 hr. and the *iodide* distilled off under reduced pressure (b. p. 62°/2 mm.). An ethereal solution of this red distillate was washed with sodium hydrogen sulphite solution, followed by sodium hydrogen carbonate solution, and finally water. Fractional distillation provided 3 : 5 : 5-trimethylhexyl iodide as a colourless oil, b. p. 68°/4 mm., $[\alpha]_D^{20}$ +11·9° ± 0·5° (*c* 3·5 in $CHCl_3$) (Found: C, 42·3; H, 7·4; I, 49·7. $C_9H_{19}I$ requires C, 42·5; H, 7·5; I, 50·0%).

meso-*Di-(3 : 5 : 5-trimethylhexyl) Phthalate*.—(+)-3 : 5 : 5-Trimethylhexyl hydrogen phthalate (2 g.), dissolved in the theoretical quantity of dilute aqueous ammonia, was treated with an excess of silver nitrate (2 g.) in water. The resultant white precipitate (2·6 g.) of silver (+)-3 : 5 : 5-trimethylhexyl phthalate was filtered off, washed with water, and dried under reduced pressure in the dark.

Excess of 3 : 5 : 5-trimethylhexyl iodide (2 g.) [from (−)-alcohol] was treated in "AnalaR" benzene (40 c.c.) with silver (+)-3 : 5 : 5-trimethylhexyl phthalate (2·6 g.), refluxed for 1 hr., cooled, and filtered. The filtrate was steam-distilled, and an ethereal solution of the residue was washed with sodium hydrogen carbonate solution, followed by water. Solvent and moisture were removed at 100° under reduced pressure and the residue, of colourless meso-*di-(3 : 5 : 5-trimethylhexyl) phthalate*, was distilled (bath 170°/0·01 mm.), to yield a colourless mobile oil, $\alpha$ 0°, which could not be crystallised (Found: C, 74·1; H, 9·8%).

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
BILLINGHAM DIVISION, CO. DURHAM.

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## 561. *Optically Active Forms of* 1-*Methyl-2-2′-pyridylethylamine.*

By N. B. CHAPMAN and J. F. A. WILLIAMS.

1-Methyl-2-2′-pyridylethyl toluene-*p*-sulphonate has been resolved through its hydrogen tartrate. Each enantiomer has been converted into the corresponding optically active form of 1-methyl-2-2′-pyridylethylamine, and these two enantiomers have been submitted for pharmacological test, especially for histamine-like action. Benzyl *N*-(±)-1-methyl-2-2′-pyridylethylcarbamate, and *N*-(−)-menthyl-*N*′-(±)-1-methyl-2-2′-pyridylethylurea are also described. A note on the resolution of racemic acid with cinchonine is included.

SEVERAL compounds which simulate the physiological action of histamine are capable of optical activity (cf. Alles, Weissburger, and Shull, *J. Pharmacol.*, **1943**, **77**, 54; Lee and Jones, *ibid.*, 1949, **97**, 71). The object of the present work was to investigate the physiological activity of the enantiomers of one of the more accessible of these compounds. We chose 1-methyl-2-2′-pyridylethylamine on grounds of accessibility (Burger and Ullyott, *J. Org. Chem.*, 1947, **12**, 342), despite the fact that this base was reported not to yield crystalline salts even with mineral acids, for clearly optical resolution presented problems of intrinsic chemical interest here.

In the event we have been unable to resolve the base by formation of diastereoisomeric salts, only the hydrogen tartrate being crystalline, but very hygroscopic and not separable into diastereoisomers by crystallisation. In order to reduce the number of possibilities of salt formation we converted the base into an acyl derivative capable of reconversion into the base by a process unlikely to cause racemisation, *viz.*, the *N*-substituted benzyl carbamate. This proved to be unstable to acids even at 0° and could not be resolved. We next prepared *N*-(−)-menthyl-*N*′-(±)-1-methyl-2-2′-pyridylethylurea, but this could not

be resolved by crystallisation or by chromatography on alumina, nor could its salts with optically active acids be separated. However, we were able to resolve a precursor of the required amine, (±)-1-methyl-2-2′-pyridylethyl toluene-*p*-sulphonate, through its hydrogen tartrate, and obtain both (+)- and (−)-1-methyl-2-2′-pyridylethyl toluene-*p*-sulphonate optically pure. The (+)- and the (−)-enantiomer were converted into (−)- and (+)-1-methyl-2-2′-pyridylethylamine respectively by the action of an excess of anhydrous ammonia at 50—60°. A more feebly basic substance formed at the same time was probably 2-propenylpyridine. We have no explicit evidence that the two enantiomers are optically pure. Partial racemisation in the amination stage is possible, though in our opinion unlikely, but because of the properties of the base it has not been possible to settle this point experimentally. The enantiomers had nearly equal optical rotations, *viz.*, $[\alpha]_D^{15}$ $+20{\cdot}7° \pm 0{\cdot}5°$ and $-22{\cdot}2° \pm 0{\cdot}5°$, the difference being perhaps due to the ready absorption of water and carbon dioxide from the air.

Preliminary pharmacological examination (unpublished) shows that (±)-1-methyl-2-2′-pyridylethylamine has histamine-like activity but is less potent than histamine, and that there is a difference in potency between the (−)- and the (+)-isomer.

## Experimental

Unless otherwise stated optical rotations were measured in methanol with $c = 1{\cdot}0$.

(±)-1-Methyl-2-2′-pyridylethylamine, prepared by Burger and Ullyott's method (*loc. cit.*), gave a *toluene*-p-*sulphonyl* derivative, m. p. 133·5—134·5° (Found: C, 61·6; H, 6·4; N, 9·9. $C_{15}H_{18}O_2N_2S$ requires C, 62·0; H, 6·2; N, 9·7%), but no crystalline salts with mineral acids (cf. Löffler and Kirschner, *Ber.*, 1905, **38**, 3329) or with (+)-camphor-10-sulphonic or (+)-camphoric acid. (+)-Tartaric acid gave a very hygroscopic salt which could be recrystallised only from dry methanol–ether.

*Benzyl* N-(±)-1-*Methyl*-2-2′-*pyridylethylcarbamate*. Benzyl chloroformate (7·65 g., 0·045 mole; Bergmann and Servas, *Ber.*, 1932, **65**, 1192) in a little acetone at 0° was added during 0·5 hr. to the foregoing amine (3·15 g., 0·023 mole) in acetone containing a trace of aqueous sodium hydroxide, the temperature being kept below 5° and the pH just alkaline by addition of aqueous sodium hydroxide. The product was brought to pH 7, acetone removed at 15 mm., 4·5N-sodium hydroxide added, and the oil formed was extracted with ether, dried ($Na_2SO_4$), and, after removal of ether, purified by extraction of neutral material from a solution in 2N-hydrochloric acid with methylene dichloride. Benzyl *N*-(±)-1-methyl-2-2′-pyridylethylcarbamate was liberated, extracted with acetone–ether (1 : 1), dried ($Na_2SO_4$), and after removal of solvents distilled (b. p. 110°/0·1 mm.); it gave a *picrate*, m. p. 136—137° (rapid heating) (Found: C, 53·0; H, 4·4; N, 13·8. $C_{22}H_{21}O_9N_5$ requires C, 53·0; H, 4·2; N, 14·0%), by the action of ethanolic picric acid on the base in ethanol at 40°.

N-(−)-*Menthyl*-N′-(±)-1-*methyl*-2-2′-*pyridylethylurea*.—(−)-Menthyl *iso*cyanate (Hardy, *J.*, 1934, 2011), b. p. 100°/14 mm., $[\alpha]_D^{20}$ −61·2° (*c*, 4·0 in $C_6H_6$), when added (7·03 g., 0·04 mole) in dry (Na) ether slowly to (±)-1-methyl-2-2′-pyridylethylamine (5·4 g., 0·04 mole) in dry ether gave N-(−)-*menthyl*-N′-(±)-1-*methyl*-2-2′-*pyridylethylurea* (89%), m. p. 123—126·5°, $[\alpha]_D^{20}$ −60·9° (*c*, 1·0 in EtOH) (Found: N, 13·0. $C_{19}H_{30}ON_3$ requires N, 13·3%). The urea was not resolved by fractional crystallisation from dry ether–acetone (1 : 4), the only solvent from which it was found to crystallise readily. The diastereoisomers were not separated by chromatography on alumina from light petroleum (b. p. 60—80°). No crystalline salts were obtained with (+)-tartaric or (+)-camphor-10-sulphonic acid.

(+)- *and* (−)-1-*Methyl*-2-2′-*pyridylethyl Toluene*-p-*sulphonate*.—(±)-1-Methyl-2-2′-pyridylethanol, b. p. 121—123°/14 mm. (*Org. Synth.*, **23**, 83) gave no crystalline salt with (+)-camphor-10-sulphonic acid, and its (+)-hydrogen tartrate was very hygroscopic. To toluene-*p*-sulphonyl chloride (7·4 g., 0·039 mole) in cold pyridine (25 g.) (±)-1-methyl-2-2′-pyridylethanol (5·2 g., 0·039 mole) was added at 0°, and the mixture was kept at *ca.* 0° for 48 hr. Sodium hydrogen carbonate (3·7 g.) was added and the mixture was stirred at 0° for 2 hr. and filtered. After removal of pyridine at 30°/15 mm., the residue was poured into water (60 c.c.), and an excess of 1·8N-sodium carbonate added. (±)-1-*Methyl*-2-2′-*pyridylethyl toluene*-p-*sulphonate* (98%) was obtained, and after recrystallisation from aqueous methanol by slow evaporation at room temperature had m. p. 83·5—85° (Found: C, 61·6; H, 5·9; N, 4·8. $C_{15}H_{17}O_3NS$ requires C, 61·8; H, 5·9; N, 4·8; S, 11·0%). It gave no crystalline salts with (+)-mandelic or (+)-camphor-10-sulphonic acid. Dissolving (+)-tartaric acid (61·6 g., 0·41

mole) in a warm solution of the racemic toluene-*p*-sulphonate (120 g., 0·41 mole) in dry ($Na_2SO_4$) acetone (4710 c.c.) gave initially a clear solution; a salt crystallised steadily during 2 hr. and (+)-1-*methyl*-2-2′-*pyridylethyl toluene*-p-*sulphonate hydrogen* (+)-*tartrate* (68·3 g.), $[\alpha]_D^{18}$ +21·7°, was obtained. Recrystallisation from dry acetone (2500 c.c.) or absolute ethanol gave material (24%) with m. p. 139—140° and $[\alpha]_D^{17}$ +35·5 ± 0·5°, unchanged by further crystallisation (Found: C, 52·0; H, 5·2; N, 2·8; S, 7·2. $C_{19}H_{23}O_9NS$ requires C, 51·7; H, 5·8; N, 3·2; S, 7·3%). Adding an excess of 1·8N-sodium carbonate to a solution of the pure hydrogen tartrate (75 g.) in 4*N*-hydrochloric acid (250 c.c.) gave (+)-1-*methyl*-2-2′-*pyridylethyl toluene*-p-*sulphonate* (100%), m. p. 70·5—71·5°, $[\alpha]_D^{18}$ +54·7 ± 0·5° (Found: C, 61·9; H, 5·8; N, 4·9; S, 10·8%). After one recrystallisation from aqueous methanol it had m. p. 70·5—72°. (−)-1-*Methyl*-2-2′-*pyridylethyl toluene*-p-*sulphonate* was obtained by a similar process with (−)-tartaric acid and a specimen of the toluene-*p*-sulphonate enriched in (−)-enantiomer, obtained as a residue in the preparation of the (+)-isomer, and had m. p. 69·5—71·5°, $[\alpha]_D^{15}$ −54·9 ± 0·5° (Found: C, 62·0; H, 5·9; N, 4·7; S, 11·1%); it gave a *hydrogen* (−)-*tartrate*, m. p. 140°, $[\alpha]_D^{15}$ −35·6 ± 0·5° (Found: C, 51·7; H, 5·1; N, 2·9; S, 7·2%). In this case an excess of aqueous ammonia (*d*, 0·88) was used to liberate the toluene-*p*-sulphonate from its hydrogen tartrate.

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(−)-*Tartaric Acid*.—In the preparation of this by Read and Reid's method (*J. Soc. Chem. Ind.*, 1928, **47**, 9T) from racemic acid and (−)-cinchonine (from the British Drug Houses Ltd.), satisfactory yields were obtained only if the (−)-cinchonine was purified by Andrews's method (*Ind. Eng. Chem. Anal.*, 1922, **14**, 543), so that it had m. p. 254—257°, and the racemic acid was crystallised until it had m. p. 203—204°. The (−)-tartaric acid was isolated through its lead salt (Haskins and Hudson, *J. Amer. Chem. Soc.*, 1939, **61**, 1266).

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THE UNIVERSITY, SOUTHAMPTON. [*Received, April* 30*th*, 1953]

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(+)- *and* (−)-1-*Methyl*-2-2′-*pyridylethylamine*.—An excess of dry (CaO) ammonia was condensed into a glass bulb containing (+)-1-methyl-2-2′-pyridylethyl toluene-*p*-sulphonate (21 g.), and the bulb was sealed and heated in a stainless steel autoclave at 45—50° for 60 hr. After ammonia had been allowed to evaporate from the cooled product, 4·5N-sodium hydroxide was added and sodium toluene-*p*-sulphonate was filtered off. An oil was extracted from the filtrate with ether, the extract dried (KOH), and the ether removed in a stream of carbon dioxide-free nitrogen, affording an oil (7·5 g.), $n_D$ 1·5280, $[\alpha]_D^{18}$ +17°, which gave a low nitrogen analysis. The amine was not purified by chromatography on ion-exchange resins or by distillation. The oil was dissolved in sufficient dilute (~0·1N) hydrochloric acid to bring the pH to 8·48, previous electrometric titration (pH meter) having established the necessary volume of acid. Feebly basic impurities were removed by four-fold extraction with an equal volume of methylene dichloride, and an excess of potassium hydroxide was added to the aqueous solution. The liberated oil was extracted with ether, the extract dried (KOH), the ether removed, and the base distilled in an atmosphere of nitrogen free from carbon dioxide, giving (−)-1-*methyl*-2-2′-*pyridylethylamine* (50%), b. p. 49°/0·016 mm., $n_D^{16}$ 1·5212, $[\alpha]_D^{15}$ −22·2° (*c*, 0·85), $[\alpha]_D^{15}$ −8·3° (*c*, 0·6 in 0·0987N-hydrochloric acid) (Found: C, 70·5; H, 8·9; N, 19·0%; neutralisation equiv. 137·2 at first neutralisation point. $C_8H_{12}N_2$ requires C, 70·6; H, 8·9; N, 20·6%; equiv. 136·2 for a monoacid base).

(+)-1-*Methyl*-2-2′-*pyridylethylamine*, b. p. 75°/0·5 mm., $[\alpha]_D^{15}$ +20·7 ± 0·5°, was similarly prepared (20%) (Found: C, 70·7; H, 8·8; N, 20·3%).

(−)-*Tartaric Acid*.—In the preparation of this by Read and Reid's method (*J. Soc. Chem. Ind.*, 1928, **47**, 9T) from racemic acid and (−)-cinchonine (from the British Drug Houses Ltd.), satisfactory yields were obtained only if the (−)-cinchonine was purified by Andrews's method (*Ind. Eng. Chem. Anal.*, 1922, **14**, 543), so that it had m. p. 254—257°, and the racemic acid was crystallised until it had m. p. 203—204°. The (−)-tartaric acid was isolated through its lead salt (Haskins and Hudson, *J. Amer. Chem. Soc.*, 1939, **61**, 1266).

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THE UNIVERSITY, SOUTHAMPTON. [*Received, April* 30*th*, 1953]

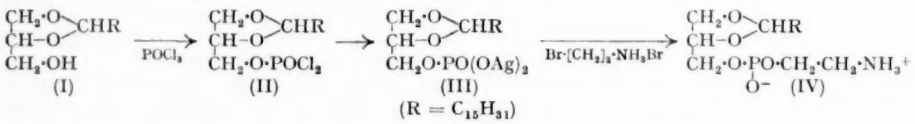
## 562. *Plasmalogens. Part I. A Synthesis of 2-Aminoethyl 2 : 3-O-Hexadecylideneglycerophosphate.*

By M. J. Egerton and T. Malkin.

An unambiguous method for the synthesis of plasmalogens is described. Long and short *X*-ray spacings of " palmital-plasmalogen " have been determined.

Plasmalogens were discovered in brain and skeletal muscles by Stepp, Feulgen, and Voit, (*Biochem. Z.*, 1927, **181**, 284), who found that on treatment with acids or mercuric chloride they yielded a steam-volatile substance; this gave an intense Schiff's reaction, and Feulgen, Imhauser, and Behrens (*Z. physiol. Chem.*, 1929, **180**, 161) found it to be a mixture of long-chain fatty aldehydes, mainly hexadecanal (palmitaldehyde) and octadecanal (stearaldehyde). Feulgen and Bersin later (*ibid.*, 1939, **260**, 217) showed that plasmalogens were acetal phosphatides, closely related to phosphatidylethanolamine, namely, 2-aminoethyl 2 : 3-*O*-hexa- or -octa-decylidene-1-glycerophosphate. Although Feulgen and Bersin obtained a mixture of 2-aminoethyl esters of 1- and 2-glycerophosphoric acid by the action of warm mercuric chloride solution on the plasmalogen, the question of the existence of the 2-glycerophosphoric isomer is an open one, owing to the well-known 1 ⟶ 2 migration of glycerophosphates: analogy with lecithin and kephalin, and the optical activity of plasmalogens, reported by Thannhauser, Boncoddo, and Schmidt (*J. Biol. Chem.*, 1951, **188**, 417), indicate the 2 : 3-acetal structure.

In 1941, Bersin, Moltmann, Nafziger, Marchand, and Leopold (*Z. physiol. Chem.*, **269**, 241) published a synthesis of the 2-aminoethyl ester of 2 : 3-*O*-hexadecylidene-1-glycerophosphoric acid, according to the scheme:




but doubts may be expressed regarding the nature of their final product. Thus, the acetal (I) was made by the direct condensation of glycerol and hexadecanal which could give rise to *cis*- and *trans*-forms of 1 : 2- and 1 : 3-acetals (cf., *e.g.*, Hibbert and Carter, *J. Amer. Chem. Soc.*, 1928, **50**, 3376; Verkade and van Roon, *Rec. Trav. chim.*, 1942, **61**, 831). The melting point was not recorded for (I), which was stated to be crystalline, and the evidence that it yielded 1-*O*-methylglycerol on methylation and hydrolysis does not appear to us to be satisfactory proof of homogeneity. Moreover, in the analogous synthesis of the 2-aminoethyl ester of phosphatidic acid (kephalin), Bevan and Malkin (*J.*, 1951, 2667) found that the action of 2-bromoethylammonium bromide on disilver phosphatidate gave only a trace of the desired product. Bersin *et al.* claim a 60% yield, but state that their product readily breaks down into plasmalogenic acid (III; H in place of Ag) and 2-hydroxyethylamine on crystallisation. This, however, is not the normal behaviour of an aminoethyl ester, and it seems probable that their product was rather a hydroxyethylamine salt, or at least, highly contaminated with this. No melting point or description was given for the synthetic product, and only nitrogen was determined.

In view of these uncertainties, we have synthesised (I) by condensing hexadecanal with α-monolaurin and removing the lauroyl group with ethanolic sodium hydroxide, to which the acetal is stable. (Protection of the 1-hydroxyl group by acetyl or benzoyl was not so satisfactory.) The acetal was then converted by phosphorus oxychloride into the plasmalogenoyl dichloride (II) which was condensed with 2'-hydroxyethylphthalimide. Removal of the phthaloyl group with aqueous hydrazine yielded a crystalline product which gave correct analyses for the plasmalogen, a positive Feulgen–Schiff's aldehyde test, and a positive ninhydrin test.

During this acetal condensation we also obtained what appears to be the geometric isomer, but as the melting points of the two pairs of isomers are very similar we prefer to reserve judgment pending *X*-ray examination.

Work on the synthesis of plasmalogens from this isomer, and from the 1 : 3-acetal is in progress.

## Experimental

1 : 2-O-*Hexadecylidene*-3-*monolaurin*.—Hexadecanal (5 g., 0·02 mole) and α-monolaurin (7 g., 0·026 mole) were heated with a little toluene-*p*-sulphonic acid at 80—90° for 4 hr. From time to time the pressure was reduced (water-pump) in order to remove the water produced. The cold product was extracted with benzene, and the extract washed with sodium hydrogen carbonate solution and water and dried ($Na_2SO_4$). After removal of the solvent, several crystallisations from benzene–ethanol yielded the *acetal* as colourless flat prisms (2 g.) which exhibited spherulite formation when viewed through a polarising microscope and had m. p. 51·5—52·5° (Found: C, 75·2; H, 12·1. $C_{31}H_{60}O_4$ requires C, 75·0; H, 12·1%). Evaporation of the mother-liquor left a residue which when recrystallised from methanol gave a crystalline *isomer* (3·5 g.) which did not exhibit spherulite behaviour and melted at 49—50° (Found: C, 75·3; H, 12·0%). The total yield of condensation product was 5·5 g. (51·8%).

1 : 2-O-*Hexadecylideneglycerol*.—The above lauroyl derivative (0·85 g.; m. p. 51·5—52·5°) was refluxed for 6 hr. with ethanol (70 ml.) containing 0·07 g. of sodium hydroxide. After removal of ethanol under reduced pressure, water was added to the residue, and the mixture was extracted with ether. The ethereal solution was well washed with water and dried ($Na_2SO_4$). After removal of the ether there remained 1 : 2-O-*hexadecylideneglycerol* as an oil which solidified at room temperature, and recrystallised from light petroleum (b. p. 40—60°) 0° as prisms (yield, *ca.* 100%), m. p. 45·5—46·5° (Found: C, 72·4; H, 12·0. $C_{19}H_{38}O_3$ requires C, 72·6; H, 12·1%).

The *isomer* (Found: C, 72·6; H, 12·0%), obtained in a similar manner from the lauroyl derivative of m. p. 49—50°, melted at 45—46°, and at 43—46° on admixture with the previous product.

2-*Aminoethyl* 2 : 3-O-*Hexadecylidene*-1-*glycerophosphate* (*Plasmalogen*).—The method of synthesis is the same as that used by Bevan and Malkin (*loc. cit.*) for the synthesis of kephalins. The apparatus should be oven-dried, and the solvents and reagents treated as follows: Chloroform to be freed from alcohol with concentrated sulphuric acid, dried ($CaCl_2$; $P_2O_5$), and distilled shortly before use. Pyridine to be dried (KOH) and fractionated. Phosphorus oxychloride to be fractionated.

To phosphorus oxychloride (342 mg., 0·0022 mole) in chloroform (2·5 ml.) in an ice-cooled 50-ml. three-necked flask fitted with mechanical stirrer, dropping funnel, and calcium chloride tube, pyridine (1 ml.) was added slowly with vigorous stirring. The flask was then placed in a bath at 10—15° and 1 : 2-*O*-hexadecylideneglycerol, m. p. 45·5—46·5° (700 mg., 0·0022 mole) in chloroform (11 ml.) and pyridine (0·11 ml.) was added dropwise with continued stirring during 1 hr. Stirring was then continued for 30 min. with the bath at 25° and for a further 30 min. at 45°. The bath-temperature was then reduced to 10—15° and 2′-hydroxyethylphthalimide (425 mg., 0·0022 mole) in chloroform (16 ml.) was added to the vigorously stirred mixture during 1 hr. Stirring was then continued at 30° and at 40° for 30 min. each. The bath-temperature was then reduced to 10—15°, and a few drops of water were added to the reaction mixture, which was then vigorously stirred for 30 min. The solvent was next removed completely (water-pump and finally mechanical pump at <40°). The residue was triturated with N-hydrochloric acid at 0—10° and filtered, the residue being washed with cold water until free from mineral acid. The precipitate (dried on a filter) was dissolved in neutral 2-methoxyethanol (25 ml.) (mechanical stirrer; <40°), and then 0·42N-sodium hydroxide (4·8 ml.) was added dropwise with vigorous stirring during 1 hr. (sufficient to form a monosodium salt on the assumption of a 90% yield of phthalimido-derivative). Hydrazine hydrate (223 mg., 0·0022 mole; 50% w/w) was added to the mechanically stirred solution, the temperature of which was slowly raised. Frothing which began to occur during the addition of sodium hydroxide ceased at this stage, and the mixture was gently refluxed for 1 hr. and left overnight. The precipitate which separated was filtered off and washed with a little neutral 2-methoxyethanol, after which it was extracted with boiling ether. The residual *plasmalogen*, recrystallised from methanol–ethanol, gave a colourless microcrystalline powder (200 mg., 21%), which softened at about 206° and formed a meniscus at 223° with some decomposition. It gave a positive blue colour

with 2% ethanolic ninhydrin and a positive Feulgen–Schiff's test (Found: C, 57·4; H, 9·8; N, 3·4. $C_{21}H_{44}O_6NP$ requires C, 57·7; H, 10·1; N, 3·2%). *X*-ray spacings: long, 38·9 Å; short, 5·64 (mod. strong, 4·54 (strong), and 3·83 Å (mod. strong).

One of us (M. J. E.) thanks the City of Gloucester Education Authority for a maintenance grant.

THE UNIVERSITY, BRISTOL. [*Received, May 14th,* 1953]

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## 563. *New Pyridine Complexes of Tellurium Tetrafluoride.*

By E. E. AYNSLEY and G. HETHERINGTON.

Tellurium tetrafluoride and pyridine in ether yield pyridinetetrafluorotellurium(IV), $(C_5H_5N)TeF_4$: this compound, with aqueous hydrofluoric acid, gives pyridinium pentafluorotellurite, $(C_5H_5NH)TeF_5$. Tellurium dioxide and pyridine in aqueous hydrofluoric acid yield dipyridinium hexafluorotellurite, $(C_5H_5NH)_2TeF_6$. Dipyridinium hexaiodotellurite is formed when any of these complex fluorides, or the hexa-chloride or -bromide, $(C_5H_5NH)_2TeX_6$, is treated with aqueous hydriodic acid.

Of these complex halides, the fluorides are the least stable, the order of stability being $[TeF_6]^-$ and $[TeF_6]^{--} < [TeCl_6]^{--} < [TeBr_6]^{--} < [TeI_6]^{--}$.

MANY double chlorides and bromides of tellurium and organic bases have been described. Lenher (*J. Amer. Chem. Soc.*, 1900, **22**, 136) prepared a series of salts of tellurium tetrabromide and tetrachloride with the hydrobromides and hydrochlorides of aliphatic and aromatic amines, the bromides being red and the chlorides invariably yellow. He made salts of the type $(C_5H_5NH)_2TeBr_6$ and $(C_5H_5NH)_2TeCl_6$ by mixing solutions of tellurium dioxide and the amine salt in the appropriate halogen acid.

Lowy and Dunbrook (*ibid.*, 1922, **44**, 614) obtained products of the type $(C_6H_5{\cdot}NH_2)_2TeBr_4$ from solutions of the amines and tellurium tetrabromide in either absolute ether or glacial acetic acid. These compounds dissolved in dilute hydrobromic acid and yielded crystalline complexes containing four molecules of the amine hydrobromide combined with one of tellurium tetrabromide, *e.g.*, $(C_6H_5{\cdot}NH_2,HBr)_4TeBr_4$. Similarly, Morgan and Burgess (*J.*, 1929, 1103) found that tellurium tetrachloride and dimethylamine, in dry ether, formed bisdimethylanilinetellurium tetrachloride, $(C_6H_5{\cdot}NMe_2)_2TeCl_4$.

No mention has, however, been found of fluorides or iodides of this series, and although fluorides of the form $M[TeF_5]$ are reported (Wells and Willis, *Amer. J. Sci.*, 1901, **12**, 190; Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, 1931, Vol. XI, p. 98) where M = Na, K, Cs, $NH_4$, or Ba; those of the type $M_2[TeF_6]$ are unknown.

We describe here the preparation of a new base, pyridinetetrafluorotellurium(IV), $(C_5H_5N)TeF_4$, and two new complex fluorides, pyridinium pentafluorotellurite, $(C_5H_5NH)TeF_5$, and dipyridinium hexafluoro- and hexaiodo-tellurite, $(C_5H_5NH)_2TeX_6$.

Dissolution of tellurium tetrafluoride and pyridine in dry ether gives white, insoluble $(C_5H_5N)TeF_4$, not $(C_5H_5N)_2TeF_4$ as might be expected by analogy with the chloride and the bromide. This compound is unchanged in dry air, but is instantly decomposed by water to tellurous acid. Above 100° it decomposes without melting. With aqueous hydrofluoric acid it gives pale green crystals of $(C_5H_5NH)TeF_5$ (I). On the other hand, in fairly concentrated aqueous hydrofluoric acid, pyridine and tellurium dioxide give buff-coloured, needle-shaped crystals of $(C_5H_5NH)_2TeF_6$ (II).

The compounds (I) and (II) are rapidly hydrolysed by water to tellurous acid, but are insoluble in and unchanged by ether. Hydrochloric acid converts both salts into dipyridinium hexachlorotellurite, $(C_5H_5NH)_2TeCl_6$; hydrobromic and hydriodic acid give

the corresponding salts (Aynsley, *J.*, in the press). Dipyridinium hexaiodotellurite also results from treatment of any of the other complex tellurium halides with hydriodic acid.

The stability of the $[TeX_6]^{--}$ anion (where X = F, Cl, Br, I) increases from the fluoride to the iodide, as illustrated by the ready conversion of any of the higher complex halides into a lower one by treatment with the appropriate halogen acid. The stability of the pentafluorotellurite anion, $[TeF_5]^-$, is of the same order as the hexafluoride anion, $[TeF_6]^{--}$; but its conversion into the lower $[TeX_6]^{--}$ anions (where X = Cl, Br, I), on treatment with the halogen acids seems to deny the existence of the chloride, bromide, and iodide of the series $(C_5H_5NH)TeX_5$, although the free acids, $HTeX_5,5H_2O$, are known (Metzner, *Compt. rend.*, 1897, **124**, 1448).

This order of stability of the complex tellurium halides, *viz.*, $[TeF_5]^-$ and $[TeF_6]^{--} < [TeCl_6]^{--} < [TeBr_6]^{--} < [TeI_6]^{--}$ is the same as that shown by Sharpe (*J.*, 1950, 3444) for the complex halides of the noble metals, *e.g.*, $[PtF_6]^{--} < [PtCl_6]^{--} < [PtBr_6]^{--}$.

## Experimental

*Pyridinetetrafluorotellurium*(IV).—Tellurium tetrafluoride was dissolved in anhydrous ether and added to a dry ethereal solution of pyridine. The resulting white precipitate of *pyridinetetrafluorotellurium*(IV) was filtered off and washed with ether, and the ether pumped off. It was analysed by dissolving it in cold sodium hydroxide solution and determining the tellurium by reducing it to the element with sulphur dioxide and hydrazine, and the fluorine by Willard and Winter's method after distillation from 50% sulphuric acid [Found: Te, 45·8; F, 26·5; C, 21·2; H, 2·2; N, 4·8. $(C_5H_5N)TeF_4$ requires Te, 45·0; F, 27·0; C, 21·3; H, 1·8; N, 5·0%].

*Pyridinium Pentafluorotellurite.*—The foregoing compound was dissolved in aqueous hydrofluoric acid, and the solution evaporated on the steam-bath until the pale green *pyridinium pentafluorotellurite* crystallised [Found: Te, 41·6; F, 31·2; C, 20·0; H, 2·0; N, 4·7. $(C_5H_5NH)TeF_5$ requires Te, 42·1; F, 31·5; C, 19·9; H, 2·0; N, 4·6%]. Treatment of this with hydrochloric acid produced yellow needles of dipyridinium hexachlorotellurite [Found: Te, 25·3; Cl, 42·6; C, 24·8; H, 2·7; N, 5·7. Calc. for $(C_5H_5NH)_2TeCl_6$: Te, 25·4; Cl, 42·6; C, 24·0; H, 2·4; N, 5·6%]. Hydrobromic acid similarly converted it into red needles of dipyridinium hexabromotellurite on recrystallisation [Found: Te, 16·4; Br, 62·5; C, 15·7; H, 1·8; N, 3·8. Calc. for $(C_5H_5NH)_2TeBr_6$: Te, 16·6; Br, 62·6; C, 15·7; H, 1·6; N, 3·7%].

On dissolution of $(C_5H_5NH)TeF_5$ in hot hydriodic acid and cooling, small, black needles of *dipyridinium hexaiodotellurite* were deposited [Found: Te, 12·9; I, 71·3; C, 11·5; H, 1·1; N, 2·1. $(C_5H_5NH)_2TeI_6$ requires Te, 12·1; I, 72·7; C, 11·4; H, 1·1; N, 2·7%].

*Dipyridinium Hexafluorotellurite.*—When pyridine was added to a solution of tellurium dioxide in aqueous hydrofluoric acid, and the solution was evaporated on the steam-bath, buff-coloured needles of *dipyridinium hexafluorotellurite* crystallised [Found: Te, 31·7; F, 28·5; C, 30·1; H, 3·0; N, 7·2. $(C_5H_5NH)_2TeF_6$ requires Te, 31·7; F, 28·4; C, 29·9; H, 3·0; N, 7·0%]. When this was treated with hydrochloric acid dipyridinium hexachlorotellurite was produced [Found: Te, 25·3; Cl, 42·3; C, 23·9; H, 2·7; N, 5·7. Calc. for $(C_5H_5NH)_2TeCl_6$: Te, 25·4; Cl, 42·6; C, 24·0; H, 2·4; N, 5·6%]. Similarly, hydrobromic and hydriodic acid afforded the corresponding hexabromo- and hexaiodo-tellurite. Also, $(C_5H_5NH)_2TeCl_6$ gave the hexabromide and hexaiodide, and $(C_5H_5NH)_2TeBr_6$, the hexaiodide, on treatment with the appropriate acid.

King's College, Newcastle-on-Tyne. [*Received, May 18th,* 1953.]

## 564. *Halogen Derivatives of Phenyl Styryl Ketone. Part I. Bromo- and Chloro-derivatives.*

By Robert D. Abell and Walter Siddall.

Contrary to other records, phenyl styryl ketone and chlorine give two stereoisomeric dichlorides, CHPhCl·CHCl·COPh; their structure is rigidly proved.

The analogous dibromide is used for an improved preparation of dibenzoylmethane.

Some incidental observations are recorded.

Two dibromides may be obtained by addition of hydrogen bromide to β-bromostyryl phenyl ketone. In 1914, at the request of the late Sir Gilbert Morgan one of us (R. D. A.) studied the preparation of dibenzoylmethane from the dibromide of m. p. 158°, by the following series of reactions:

(*a*) $CHPhBr{\cdot}CHBr{\cdot}COPh + KOAc \longrightarrow CHPh{:}CBr{\cdot}COPh + KBr + AcOH$
(*b*) $CHPh{:}CBr{\cdot}COPh + NaOEt \longrightarrow EtO{\cdot}CPh{:}CH{\cdot}COPh + NaBr$
(*c*) $EtO{\cdot}CPh{:}CH{\cdot}COPh + H_2O \longrightarrow Ph{\cdot}CO{\cdot}CH_2{\cdot}COPh + EtOH$

Reaction (*a*) was complete within 30 minutes at the boiling point, and reaction (*b*) within 10 minutes; on the basis of these observations it was possible to prepare dibenzoylmethane from 92-g. batches of the dibromide in an overall yield of 81·4% in a total time of 45 minutes; this is in both respects superior to the claims in *Org. Synth.*, **8**, p. 60 (cf., *inter al.*, Pond, Maxwell, and Norman, *Amer. Chem. J.*, 1899, **21**, 964; Pond, Yorke, and Moore, *ibid.*, 1901, **23**, 798; *Org. Synth.*, **20**, p. 32).

Goldschmidt (*Ber.*, 1895, **28**, 2540) had reported the preparation of a dichloride, m. p. 113°, by addition of chlorine to phenyl styryl ketone. We have resolved this well-defined material by fractional crystallisation into two stereoisomers, m. p. 116° and 99° respectively, in proportions of about 9 : 1. The material of m. p. 113° appears to be a molecular compound, as also do two other sets of crystals, of different forms, which melt sharply at 82—83° and 87°. Jackson and Pasint (*J. Amer. Chem. Soc.*, 1927, **49**, 2071) obtained the materials of m. p. 82—83°, 98—99°, and 113—114°, and von Auwers and Hügel (*J. pr. Chem.*, 1935, **143**, 159) also studied the reaction, but the pure isomers appear not to have been recorded before. Both isomers react with alcoholic potassium acetate to give β-chlorostyryl phenyl ketone and, quantitatively, potassium chloride and acetic acid. The unsaturated ketone and phenylmagnesium bromide give quantitatively α-chloro-ββ-diphenylpropiophenone, which was also obtained from ethyl α-chlorocinnamate and phenylmagnesium bromide, thus proving the structures of the unsaturated chloro-ketone and thence also of the stereoisomeric dichlorides, CHPhCl·CHCl·COPh.

β-Chlorostyryl phenyl ketone does not recombine with hydrogen chloride as β-bromostyryl phenyl ketone does with hydrogen bromide. But it adds bromine, to give αβ-dibromo-α-chloro-β-phenylpropiophenone, CHPhBr·CClBr·COPh. Its addition of hydrogen bromide is discussed in the following paper.

In the Experimental section we record reactions of the mono- and di-bromo-compounds with ketonic reagents, the products from the unsaturated ketones varying according to the conditions.

### Experimental

*Preparation of Dibenzoylmethane.*—According to *Org. Synth.* (*loc. cit.*), dibenzoylmethane is prepared from the dibromide, m. p. 158°, in an overall yield of 59—61% in two stages occupying 5 hr. After a study of the stages (*a*—*c*) above in detail, partly with Miss G. Fell, the following procedure was standardised.

The dibromide (92 g.), potassium acetate (35 g.), and absolute alcohol (300 c.c.) were heated under reflux for 1 hr. To the cooled mixture N-ethanolic sodium ethoxide (500 c.c.) was added and the whole boiled for 10 min., a trace of alkalinity remaining. Acetic acid (10 c.c.) was

added and most (700 c.c.) of the alcohol distilled off. Addition of water then precipitated α-ethoxystyryl phenyl ketone. The supernatant liquid was decanted and extracted twice with ether, the ethereal extracts being then used to collect the oily ethoxy-derivative. Removal of the ether gave a residual oil which was heated to boiling with alcohol (30 c.c.) and concentrated hydrochloric acid (10 c.c.), with vigorous shaking, for 5 min. Addition of water (150 c.c.) and cooling, with shaking, gave dibenzoylmethane as a granular mass which was filtered off. The filtrate was extracted with ether and the extract freed from acid and treated with copper acetate solution, to afford 0·5 g. of the copper derivative. The crude dibenzoylmethane, recrystallised from the minimum of alcohol, gave 41·5 g. of the pure product, m. p. 77—78°; the recrystallisation liquors afforded 4·2 g. of the copper compound. The total yield was 81·4%.

*Recovery from the copper derivative.* Wislicenus (*Annalen*, 1899, **308**, 345) recovered dibenzoylmethane from its copper derivative by heating the latter with hydrochloric acid but this involves loss by hydrolysis to benzoic acid and acetophenone. 33% Sulphuric acid is slower in action but causes more hydrolysis.

A rapid method is to shake the derivative with ether and concentrated hydrochloric acid, wash and evaporate the ethereal solution, and recrystallise the residue from alcohol. The product is, however, always a deep pink.

Passage of hydrogen sulphide into a hot alcoholic suspension of the copper derivative, storage to permit coagulation of copper sulphide, filtration, and washing of the solid with hot alcohol gave, from the cooled filtrate, pale yellow crystals, m. p. 77—78°. The mother-liquors yielded, on concentration, a further small quantity.

*αβ-Dichlorostyryl Phenyl Ketone.*—Saturation of a cold solution of phenyl styryl ketone in chloroform, ether, carbon disulphide, or acetic acid with chlorine, and working up in the usual way, gave crystals melting sharply at 113° (cf. Goldschmidt, *loc. cit.*). Crystallisation of a not too concentrated alcoholic solution of these gave the *dichloride* as short needles, m. p. 116° unaltered by recrystallisation from the same or other solvents (Found: Cl, 25·4. $C_{15}H_{12}OCl_2$ requires Cl, 25·45%). Further concentration gave, first, material of the same m. p. (116°), and then crystals which melted at 82—83°, 87°, or 113° (cf. Jackson and Pasint, *loc. cit.*). The crystals and liquor were then united and evaporated to dryness in a vacuum-desiccator over sulphuric acid. A warm, not too concentrated methyl-alcoholic solution of the residue yielded, on cooling, the *isomer* as prisms, m. p. 99° (Found: Cl, 25·4%). Concentration of the methyl-alcoholic mother-liquors yielded further crops of m. p. 99°, but later crystals of m. p. 82—83 or 87°. Alternation of crystallisation from ethyl and methyl alcohol permitted separation of all the material into the isomers of m. p. 116° (9 parts) and 99° (1 part), almost without loss; but solvents must be anhydrous and the evaporations conducted without heat, in order to prevent hydrolysis which is even more rapid than with the corresponding dibromides (Abell, *loc. cit.*).

*Conversion of the Dichloride into β-Chlorostyryl Phenyl Ketone.*—Each of the dichlorides, when heated under reflux with potassium acetate (1·25 mols.) in ethyl alcohol for 0·5 hr., gave (i) quantitatively, potassium bromide and acetic acid (for determination see above) and (ii) β-chlorostyryl phenyl ketone, b. p. 214°/13 mm., m. p. 40° (from light petroleum) (Found: Cl, 14·5. Calc. for $C_{15}H_{11}OCl$: Cl, 14·6%); von Auwers and Hügel (*loc. cit.*) obtained the ketone only as an oil, b. p. 204—205°/10 mm. The chlorostyryl phenyl ketone and phenylmagnesium bromide gave α-chloro-ββ-diphenylpropiophenone, m. p. 144°.

During analysis of α-chloro-ββ-diphenylpropiophenone by Stephanow's method an unidentified acid was obtained as pale yellow plates, m. p. 246° (decomp.), almost insoluble in water; this acid is obtained in approx. 20% yield when this chloro-ketone or its bromo-analogue is heated with alcoholic sodium ethoxide or hydroxide or potassium hydroxide.

*αβ-Dibromo-α-chloro-β-phenylpropiophenone.*—β-Chlorostyryl phenyl ketone and bromine in carbon disulphide give the *trihalogeno-ketone*, m. p. 102° (Found: Br, 39·65; Cl, 8·8. $C_{15}H_{11}OClBr_2$ requires Br, 39·75; Cl, 8·8%).

*Reactions with Hydroxylamine.*—(a) *αβ-Dibromo-β-phenylpropiophenone.* The dibromide, m. p. 158° (3·65 g.), and hydroxylamine hydrochloride (0·7 g.) in alcohol (100 c.c.) were boiled for 2 hr., yielding the oxime, m. p. 156° (Found: N, 3·65. Calc. for $C_{15}H_{13}ONBr_2$: N, 3·7%); this was also obtained by addition of bromine to phenyl styryl ketoxime (Rupe and Schneider, *Ber.*, 1895, **28**, 965). At slightly above the m. p. the oxime yields 3 : 5-diphenyl*iso*oxazole, m. p. and mixed m. p. 140°, and 2 mols. of hydrogen bromide.

The dibromide, m. p. 122°, similarly gave an *oxime*, m. p. 113° (Found: N, 3·6%), which decomposes above the m. p. into hydrogen bromide and 3 : 5-diphenyl*iso*oxazole.

(*b*) *αβ-Dichloro-β-phenylpropiophenone.* The dichlorides, m. p. 116° and 99°, similarly gave their *oximes*, m. p. 157° (Found: N, 4·7. $C_{15}H_{13}ONCl_2$ requires N, 4·7%), and 83° (Found:

N, 4·6%), respectively. Both oximes gave, above the m. p., hydrogen chloride and 3 : 5-diphenyl*iso*oxazole, m. p. and mixed m. p. 140°.

(c) β-*Bromostyryl phenyl ketone.* When β-bromostyryl phenyl ketone similarly (4 hr. at the b. p.) gave the oxime, m. p. 151° (cf. von Auwers, *Ber.*, 1929, **62**, 1320); which with hot alcoholic alkali gave 3 : 5-diphenyl*iso*oxazole, m. p. and mixed m. p. 140°.

When the solution was made just alkaline to phenolphthalein (pH 9) before being heated, only 3 : 5-diphenyl*iso*oxazole was produced.

When an alcoholic solution of hydroxylamine hydrochloride was neutralised to methyl-orange (pH 4), treated with less than 1 mol. of β-bromostyryl phenyl ketone, and set aside at room temperature for several days (preliminary warming is permissible but the solution must not be boiled), crystals were deposited which yielded, from alcohol or light petroleum, α-*bromo*-β-*hydroxyamino*-β-*phenylpropiophenone* as rhombs, m. p. 199°, which slowly reduce warm Fehling's solution (Found : N, 4·25. $C_{15}H_{14}O_2NBr$ requires N, 4·4%).

(d) β-*Chlorostyryl phenyl ketone.* This ketone, at pH 1 (2 hr.), gave the *oxime* as prisms, m. p. 156° (Found : N, 5·4; Cl, 13·7. $C_{15}H_{12}ONCl$ requires N, 5·4; Cl, 13·8%).

Neutralisation, as in (c) above, to phenolphthalein gave 3 : 5-diphenyl*iso*oxazole, m. p. and mixed m. p. 140°.

Reaction in solution neutral to methyl-orange at room temperature, as in (c) above, gave α-*chloro*-β-*hydroxyamino*-β-*phenylpropiophenone*, m. p. 133—134° (Found : N, 5·1. $C_{15}H_{14}O_2NCl$ requires N, 5·1%), soluble in 2N-sodium hydroxide or warm dilute hydrochloric acid. The compound reduces warm Fehling's solution but is unaffected by warm formic acid.

*Reactions with Hydrazine.*—Mixing β-bromostyryl phenyl ketone and hydrazine hydrate in alcohol caused an exothermic reaction. The solution deposited 3 : 5-diphenylpyrazole as prisms, m. p. and mixed m. p. 199° (Found : N, 12·8. Calc. for $C_{15}H_{12}N_2$ : N, 12·7%) (cf. Wislicenus, *Annalen*, 1899, **308**, 219; Knorr and Duden, *Ber.*, 1883, **16**, 115).

Similar treatment of β-chlorostyryl phenyl ketone caused transitory appearance of needles (? the hydrazone) and then the above pyrazole, m. p. and mixed m. p. 199° (Found : N, 12·8%), as sole final product.

*Reactions with Phenylhydrazine.*—(a) β-*Bromostyryl phenyl ketone.* The bromo-ketone and phenylhydrazine in acetic acid on the water-bath for 1 hour, gave only 1 : 3 : 5-triphenylpyrazole, m. p. and mixed m. p. 136—137°. Heating for only 1 min. afforded a mixture, m. p. 110—126°, whereas treatment with hot alcohol separated a small amount of the sparingly soluble, orange-yellow *phenylhydrazone*, m. p. 114—115° (Found : N, 7·5; Br, 21·0. $C_{21}H_{17}N_2Br$ requires N, 7·4; Br, 21·2%). The soluble material from the mother-liquors yielded 1 : 3 : 5-triphenylpyrazole, m. p. and mixed m. p. 136°, when warmed with potassium hydroxide solution.

Heating the bromo-ketone and phenylhydrazine in ether under reflux for 15 min. gave a mixture of 1 : 3 : 5-triphenylpyrazole, prisms, m. p. and mixed m. p. 136°, and the less soluble α-*bromo*-β-*phenyl*-β-*phenylhydrazinopropiophenone phenylhydrazone*, plates, m. p. 210—211°, which darken in air (Found : N, 11·6; Br, 16·4. $C_{27}H_{25}N_4Br$ requires N, 11·55; Br, 16·5%).

(b) β-*Chlorostyryl phenyl ketone.* When heated with phenylhydrazine in alcohol and acetic acid for 2 hr., the chloro-ketone gave 1 : 3 : 5-triphenylpyrazole, m. p. and mixed m. p. 137°.

Boiling the chloro-ketone with phenylhydrazine in ether under reflux for 1 hr. gave the yellow *phenylhydrazone*, m. p. 152° (decomp. at 165°) (Found : N, 8·5; Cl, 10·7. $C_{21}H_{17}N_2Cl$ requires N, 8·4; Cl, 10·7%), which with alcoholic alkali gave 1 : 3 : 5-triphenylpyrazole. There was no evidence of formation of the phenylhydrazino-phenylhydrazone [cf. (a) above].

*Reactions with 2 : 4-Dinitrophenylhydrazine.*—By Brady's method (*J.*, 1931, 757; 2 min.' warming), β-*bromostyryl phenyl ketone* 2 : 4-*dinitrophenylhydrazone* was obtained as yellowish-red rhombs, m. p. 181°, in rather poor yield (Found : N, 11·8%. $C_{21}H_{15}O_4N_4Br$ requires N, 12·0%).

The β-*chloro-ketone* 2 : 4-*dinitrophenylhydrazone*, similarly prepared, had m. p. 242° (Found : N, 13·3; Cl, 8·3. $C_{21}H_{15}O_4N_4Cl$ requires N, 13·2; Cl, 8·4%), which is stable to boiling acetic acid as the nitro-groups prevent ring-closure (cf. von Auwers and Voss, *loc. cit.*, 1929).

*Reactions with Semicarbazide.*—(a) β-*Bromostyryl phenyl ketones.* The ketone and semicarbazide hydrochloride in alcohol, made just alkaline to phenolphthalein (pH 9), afforded only 3 : 5-diphenylpyrazole, m. p. and mixed m. p. 199°. Reaction at pH 1, alone or with an excess of potassium acetate (1 hr. at the b. p.), gave a mixture, separated by means of alcohol into (i) a small quantity of sparingly soluble crystals which softened and decomposed above 300° (possibly the semicarbazidosemicarbazone), (ii) 3 : 5-diphenylpyrazole, m. p. and mixed m. p. 199°, and (iii) the *semicarbazone*, yellow needles, m. p. 176—177° (Found : N, 12·1; Br, 22·8. $C_{16}H_{14}ON_3Br$ requires N, 12·2; Br, 23·3%). With warm alcoholic potassium

hydroxide, the semicarbazone gave 3 : 5-diphenylpyrazole, potassium bromide, and ammonia, and with boiling aqueous-alcoholic hydrochloric acid gave the pyrazole, carbon dioxide, and ammonium chloride and bromide.

(b) *β-Chlorostyryl phenyl ketone.* The chloro-ketone and semicarbazide hydrochloride in boiling alcohol gave, in 3 hr., 3 : 5-diphenylpyrazole, m. p. and mixed m. p. 199°, as sole product. Reaction at pH 4 gave the *semicarbazone* as rhombs (from alcohol), m. p. 179—180° (Found : N, 14·25; Cl, 11·6. $C_{16}H_{14}ON_3Cl$ requires N, 14·0; Cl, 11·85%) (behaviour with alkali and acid as for the bromo-analogue), and from the mother-liquors a small amount of needles, m. p. 237—246° (possibly the semicarbazidosemicarbazone). The latter product, m. p. 246°, was also obtained in small yield when the ketone, hydrochloride, and potassium acetate were boiled in 70% alcohol (100 c.c.) for 1 hr.

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## 565. *Halogen Derivatives of Phenyl Styryl Ketone. Part II.* Bromo-chloro-derivatives. Two Cases of "Extra" Isomers.*

By ROBERT D. ABELL.

The ketones, CHPhBr·CHCl·COPh and CHPhCl·CHBr·COPh, are each obtained in three optically inactive isomeric forms though only two are to be expected on the basis of two asymmetric atoms. The structure of each of the triads appears to be rigidly established and there is no evidence of polymorphism. The "extra" isomers may owe their existence to restricted rotation about the single α–β carbon–carbon bond.

ADDITION of hydrogen bromide to β-chlorostyryl phenyl ketone occurs readily in carbon disulphide solution :

$$CHPh{:}CCl{\cdot}COPh + HBr \longrightarrow CHPhBr{\cdot}CHCl{\cdot}COPh \quad (I)$$

Three isomers, m. p. 106°, 124°, and 134°, respectively, were separated by fractional crystallisation. When heated with potassium acetate in alcohol, each isomer gave β-chlorostyryl phenyl ketone and, quantitatively, bromide ion with no trace of chloride :

$$CHPhBr{\cdot}CHCl{\cdot}COPh + KOAc \longrightarrow CHPh{:}CCl{\cdot}COPh + KBr + AcOH$$

Each isomer therefore appears unequivocally to have the structure (I).

Hydrogen chloride does not add to β-bromostyryl phenyl ketone. However, bromine chloride added to phenyl stryyl ketone, to give three isomers (II), m. p. 93°, 135—136°, and 144—145°, respectively :

$$CHPh{:}CH{\cdot}COPh + BrCl \longrightarrow CHPhCl{\cdot}CHBr{\cdot}COPh \quad (II)$$

Potassium acetate in boiling alcohol yielded from each isomer β-bromostyryl phenyl ketone with, quantitatively, chloride ion and no trace of bromide :

$$CHPhCl{\cdot}CHBr{\cdot}COPh + KOAc \longrightarrow CHPh{:}CBr{\cdot}COPh + KCl + AcOH$$

Structure (II) thus seems firmly established for each of these isomers.

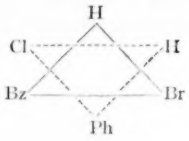
The isomers gave depressions of the melting point when mixed in pairs. During an extremely extensive series of crystallisations no transformation of one form into another was observed. The melting points have remained unchanged after storage for many years, those of (I) for more than 40 years and those of (II) for more than 10 years. There is thus no evidence of polymorphism.

When boiled with hydroxylamine hydrochloride and a drop of hydrochloric acid the isomers slowly lose hydrogen halide (the same halide as with potassium acetate); in one case of such slightly incomplete hydrolysis of the chlorobromo-compound (I), m. p. 106°,

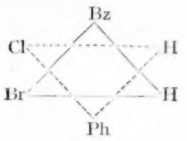
* Part I, preceding paper.

the small amount of recovered (I) had m. p. 134°. This was the sole transformation achieved. In all similar experiments with this or the other isomers, of (I) or of (II), the recovered material was unchanged in melting point.

Since the compounds (I) and (II) have each two different asymmetric carbon atoms, two optically inactive forms of each are to be expected. In each case, however, three forms have been obtained. The extra form may owe its existence to restricted rotation about the single α–β carbon–carbon bond, cf. (III)—(IV) which represent the same diastereoisomer.




(III)




(IV)

(III) Could lose HCl to give the *cis*-form of PhCH=CBr·Bz—m.p. 44°.
(IV) Could not be expected to lose either HCl or HBr.

It must be noted however that modern methods of separating similar substances were not available when this work was done. It should be noted that the ketone group appears to be sterically hindered, insofar as no oxime could be obtained.

## Experimental

Analytical values for bromine and chlorine in the same compound are based on determination of total halogen by Stepanow's method and calculation therefrom on the assumption of equimolar content of the two halogens.

*β-Bromo-α-chloro-β-phenylpropiophenone.*—A solution of β-chlorostyryl phenyl ketone (20 g.) in carbon disulphide (100 c.c.) was saturated with dry hydrogen bromide. After 12 hr. the solvent and excess of acid were removed in a stream of dry air, leaving a colourless crystalline mixture (26·5 g.) which was separated by means of methyl and ethyl alcohols into the following isomers of *β-bromo-α-chloro-β-phenylpropiophenone*: A, prisms (19·0 g.), m. p. 124°, moderately soluble in hot ethyl alcohol, sparingly soluble in cold ethyl alcohol (much less so than isomers B and C) (Found: Cl, 11·0; Br, 24·7. $C_{15}H_{14}OClBr$ requires Cl, 11·0; Br, 24·7%); B, prisms (1·5 g.), m. p. 134°, less readily soluble than C in warm methyl alcohol (Found: Cl, 10·9; Br, 24·65%); and C, fine needles (3·0 g.), m. p. 106° (Found: Cl, 10·9; Br, 24·7%). A residual, more soluble yellow oil (2·5 g.) gradually crystallised, then having m. p. 40° and being identified (mixed m. p.) as β-chlorostyryl phenyl ketone. It is impossible to prescribe a simple scheme of separation, very many operations being required to achieve the yields given above, but the general method will be apparent from the relative solubilities noted above; it is essential that the alcohols be anhydrous and that anhydrous conditions be maintained throughout, in order to minimise hydrolysis—it is hydrolysis, rather than incomplete reaction, which accounts for the "recovered" β-chlorostyryl phenyl ketone.

After treatment of each isomer with an excess of potassium acetate in boiling alcohol for 0·5 hr., Volhard determination demonstrated quantitative liberation of bromide ion, and chloride ion was absent. The β-chlorostyryl phenyl ketone produced had m. p. and mixed m. p. 40°, and its identity was confirmed by quantitative formation of α-chloro-ββ-diphenylpropiophenone, m. p. and mixed m. p. 144°, on reaction with phenylmagnesium bromide.

*α-Bromo-β-chloro-β-phenylpropiophenone.*—A (standardised) solution of bromine chloride in carbon disulphide or glacial acetic acid was decolorised instantly and exothermally on admixture with an excess of phenyl styryl ketone in the same solvent. On cooling, the solution deposited a large quantity of a crystalline mixture which, when washed with alcohol, melted sharply at 128° (Found: Cl, 11·05; Br, 24·7%). Many crystallisations from various solvents separated the following isomers of *α-bromo-β-chloro-β-phenylpropiophenone*: A, m. p. 144—145° (from alcohol) (Found: Cl, 11·0; Br, 24·7%); B, m. p. 135—136° (from alcohol or light petroleum) (Found: Cl, 11·0; Br, 24·7%); and C, m. p. 93° (Found: Cl, 10·9; Br, 24·6%). It is impossible to prescribe a solvent technique for this separation: only partial separation was achieved in 2 years of experimentation. These isomers are notably less easily hydrolysed by aqueous alcohol than are the β-bromo-α-chloro-compounds.

Each isomer, when dehydrohalogenated as above, gave halide ion quantitatively, which was

only chloride; the β-bromostyryl phenyl ketone produced had m. p. and mixed m. p. 44° and with phenylmagnesium bromide gave quantitatively α-bromo-ββ-diphenylpropiophenone, m. p. and mixed m. p. 163°.

*Isomerisation.*—β-Bromo-α-chloro-β-phenylpropiophenone, m. p. 106° (2 g.), hydroxylamine hydrochloride (1 g.), and concentrated hydrochloric acid (1 drop) in alcohol (25—30 c.c.) were heated under reflux for 4 hr. and then set aside overnight. Next morning a considerable crop of unchanged isomer, m. p. and mixed m. p. 106°, had crystallised and was collected. A second similar treatment of the recovered material gave a reduced amount of the same recovered isomer. A third similar treatment reduced the amount still further, but the melting point remained the same. A fourth similar treatment gave only a few crystals and these had m. p. 134°, alone or mixed with the isomer of that m. p.

Similar experiments with the other five isomers gave only unchanged material until all had been decomposed.

No oximes could be obtained.

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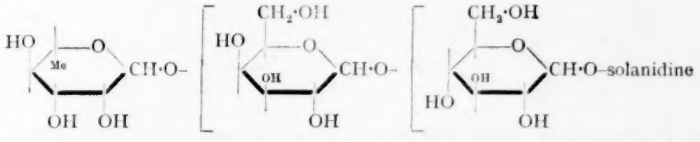
## 566. Solanum *Alkaloids. Part X.* The Mode of Linkages in the Trisaccharide Moiety of Solanine and Solasonine.*

By Lindsay H. Briggs, and L. C. Vining.

Periodate oxidation of solanine shows that the three sugars, L-rhamnose, D-galactose, and D-glucose, of the trisaccharide moiety are probably linked in the **1, 1 : 4**, and **1 : 6**, position respectively. Solasonine reacts similarly and must contain the same trisaccharide. The interpretation of the results has been assisted by comparison with the quantitative periodate oxidation of amygdalin. Oxidation of rutin goes beyond the expected values, indicating that the flavonol nucleus is also attacked. 1-Hydroxyanthraquinone is oxidised by periodate to 1 : 4-dihydroxyanthraquinone.

Solanine on hydrolysis affords the aglycone, solanidine, and three sugars, L-rhamnose, D-galactose, and D-glucose (Zwenger and Kind, *Annalen*, 1859, **109**, 244; 1861, **118**, 129; 1865, **123**, 341; Schulz, *Z. Zuckind. Böhm.*, 1900, **25**, 89; Zeisel and Wittmann, *Ber.*, 1903, **36**, 3554; Votoček and Vondraček, *ibid.*, p. 4372; Heiduschla and Sieger, *Arch. Pharm.*, 1917, **255**, 18). Since solanidine is a tertiary base with the only oxygen atom present as a hydroxyl group at $C_{(3)}$ (Prelog and Szpilfogel, *Helv. Chim. Acta*, 1942, **25**, 1306; Uhle and Jacobs, *J. Biol. Chem.*, 1945, **160**, 243) the three sugars must form a trisaccharide combined with this hydroxyl group. From a study of the acetylated glycoside Zemplén and Gerecs (*Ber.*, 1928, **61**, 2294) showed that solanine is constituted in the order of components, rhamnose–galactose–glucose–solanidine. Solanine has no reducing properties so that the three sugars must be linked through their potential aldehyde groups. Solanine is not hydrolysed, as shown by the lack of reducing power towards Fehling's solution, when treated with 0·01N-hydrochloric acid for 7 hr. From this we assume that all the sugars are pyranose (cf. Haworth, *Ber.*, 1932, **65**, *A*, 50) and the following schematic formula illustrates the trisaccharide moiety of solanine.




Neglecting the α- or β-nature of the sugar linkages for the moment it may be seen that there are **16** possible ways of combining the sugars in the order and manner given.

* Part IX, *J.*, 1952, 3591.

Since the discovery by Malaprade (*Compt. rend.*, 1928, **186**, 382) that periodic acid oxidises glycols and triols quantitatively, the method has been used extensively for the elucidation of sugar structures (cf. *Org. Reactions*, 1944, **2**, 341—375). Solasodine, and presumably solanidine, is not oxidised to any appreciable extent by periodic acid but solanine is readily oxidised at 25°.

The number of mols. of periodic acid which would be consumed, and of formic acid produced, by each of the 16 possible combinations of sugars in solanine ranges from 2 and 1 to 6 and 3. Experiment (Fig. 1) shows that 5 mols. of periodic acid are consumed and

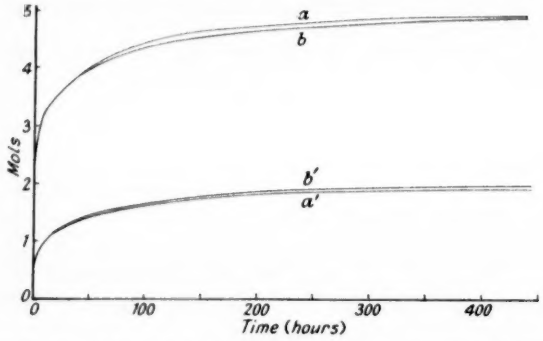
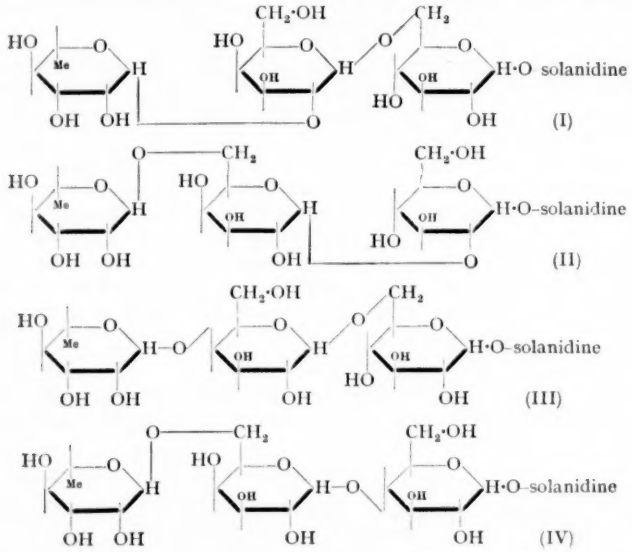



FIG. 1. *Periodate Oxidation of* (*a*) *Solanine and* (*b*) *Solasonine at* 25°.
Top curves : Periodate consumed.
Lower curves : Formic acid produced.

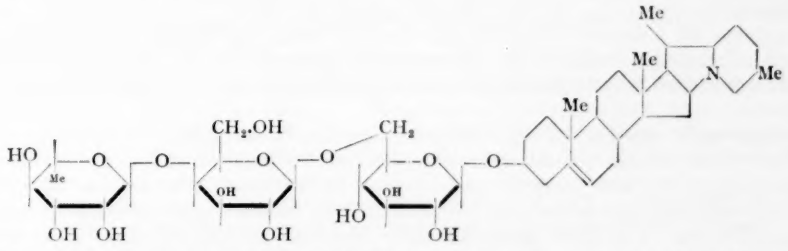
2 mols. of formic acid are produced, limiting the possibilities to four, *viz.*, (I) monosaccharide linkages 1, 1 : 2, 1 : 6, (II) 1, 1 : 6, 1 : 2, (III) 1, 1 : 4, 1 : 6, and (IV) 1, 1 : 6, 1 : 4. Structures involving a 1 : 2′-linkage are extremely rare in Nature, only three examples being recorded [sophorose (2-D-glucosyl β-D-glucoside) (Rabaté, *Bull. Soc. chim.*, 1940, **7**, 565; Freudenberg, Knauber, and Cramer, *Chem. Ber.*, 1951, **84**, 144; Gakhokidze, *J. Gen. Chem. U.S.S.R.*, 1941, **11**, 117); 2-L-rhamnosyl D-galacturonide (Tipson, Christman,




and Levene, *J. Biol. Chem.*, 1939, **128**, 609); apiin (Hemming and Ollis, *Chem. and Ind.*, 1953, 85)]. Although the combinations (I) and (II) with 1 : 2-linkages cannot be excluded at this stage (they will be excluded on later evidence), the most likely structures are (III) and (IV).

Now (III) and (IV) can be differentiated by the rates of reaction at 25°. Both contain the same *cis-trans*-triol of rhamnose and further *trans*-glycols in the galactose and glucose portions severally. In addition, (III) contains a further *trans-trans*-triol whereas (IV) contains another *cis-trans*-triol. Price *et al.* (*J. Amer. Chem. Soc.*, 1938, **60**, 2726; 1942, **64**, 552) have shown that *cis*- and *trans*-glycols react with periodic acid at markedly different rates and the same is presumably true in regard to *cis-trans*- and *trans-trans*-triols. It is certainly true in the case of oxidations with lead tetra-acetate which has a similar action (cf. Freudenberg and Rogers, *ibid.*, 1937, **59**, 1602; Richtmyer, Carr, and Hudson, *ibid.*, 1943, **65**, 1477; Hockett and McClenahan, *ibid.*, 1939, **61**, 1667). In certain triols the consumption of the second mol. of lead tetra-acetate is influenced by the possibility of lactol formation from the hydroxy-dialdehyde formed by the initial action of the first mol. (cf. Helferich, *Ber.*, 1931, **64**, 104; Hockett and McClenahan, *J. Amer. Chem. Soc.*, 1938. **60**. 2061; Hockett, Dienes, and Ramsden, *ibid.*, 1943, **65**, 1474; Hockett, Nickerson, and Reeder, *tert., ibid.*, 1944, **66**, 472). In the present case no α-hydroxy-lactol formation is possible with the combinations (III) and (IV) and, on the assumption that the action of periodate follows that of lead tetra-acetate, the rate of oxidation should be governed mainly by the configuration of the triol groupings.

Since the triol portions of the molecule are responsible for the production of formic acid, it would be expected that in (IV), with two similar triol groupings, the two mols. of formic acid would be produced at approximately the same rate. On the other hand, with (III), which has two different triol groupings, the rates would be expected to differ. Fig. 1 shows clearly that the two mols. of formic acid are produced at greatly differing rates, from which it may be concluded that the combination of sugars in solanine is probably represented by (III). No evidence can be adduced from these experiments relating to the α- or β-linkages of the sugars, but from the ease of hydrolysis of solanine with 2% mineral acids they are all probably β. Solanine may then be tentatively represented by the annexed formula.




Oddo and Caronna's work (*Ber.*, 1934, **67**, 446, and earlier papers) and results recorded in Part II (*J.*, 1942, 3) showed that solasonine also contains a trisaccharide moiety consisting of the same sugars, L-rhamnose, D-galactose, and D-glucose, joined in the same order as in solanine to the hydroxyl group at $C_{(3)}$ of the aglycone, solasodine, represented by a revised formulation in Part V (*J.*, 1950, 3013). Solasonine, like solanine, has no reducing properties, so that the sugars must be joined through their potential aldehyde groups. The sugar linkages are all probably β, from the relative ease of hydrolysis with 2% mineral acids. Solasonine is, however, not hydrolysed, as shown by the lack of reducing power towards Fehling's solution, when treated with 0·01N-hydrochloric acid for 4½ hours, from which we again assume that the sugars are pyranose.

Periodate oxidation of solasonine at 25° afforded results (Fig. 1) practically indistinguishable from those of solanine, so that both probably contain the same trisaccharide. Solasonine may then be represented similarly to solanine. The formula for solasonine given in Part V illustrates the glucose unit with a β-linkage. This was based only on the phytochemical ground that most glucosides have a β-linkage.

Solauricine (Part IV, *J.*, 1942, 17) on hydrolysis affords the aglycone solauricidine, possibly an epimer of solasodine about $C_{(22)}$ (Part V, *loc. cit.*), and the same three sugars as above. It is most likely that the trisaccharide moiety is the same as that of solanine

and solasonine and, in our opinion, therefore, solauricine is identical with solasonine, apart from the epimerisation at $C_{(22)}$.

The trisaccharide discussed in this paper is found only in members of the *Solanum* species and the name, solanose, is proposed for it. A different trisaccharide, L-rhamnose-L-rhamnose-D-glucose, occurs combined with solasodine in solamargine, from *Solanum marginatum* (Part VIII, *J.*, 1952, 3587, and forthcoming communication).

Further support for the structure of the trisaccharide was sought by oxidation and hydrolysis of the intermediate hexa-aldehyde obtained by periodate oxidation, and identification of the final fragments, by the procedure developed and applied by Hudson and his co-workers (cf. Richtmyer and Hudson, *J. Org. Chem.*, 1946, **11**, 610). Either of the structures, (III) or (IV), for solanine (or corresponding formulæ for solasonine) should, on complete periodate oxidation, give rise to a hexa-aldehyde capable of oxidation to the hexacarboxylic acid with bromine water. Hydrolysis of the hexa-acid should then give

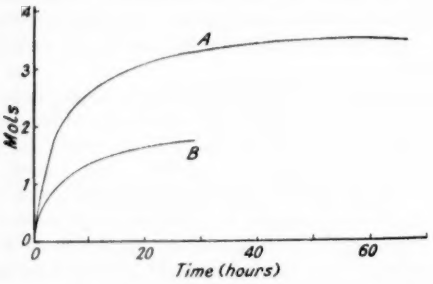
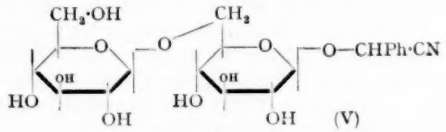



FIG. 2. *Periodate oxidation of amygdalin at* 25°.
*A*, Periodate consumed.
*B*, Formic acid produced.

four fragments, identical in three cases (L-lactic, glyoxylic, and D-glyceric acid) but differing in the fourth component, D-threonic acid arising from (III) and the epimeric D-erythronic acid from (IV).

Structures for solanine and solasonine derived from combinations (I) and (II), containing 1 : 2′-linkages, could not by the same procedure yield either threonic or erythronic acid but would give a hydroxymalonic acid in addition to the other three acids mentioned above.

By systematic analysis of the final mixture of acids through their sparingly soluble metal salts (for details, see Experimental section) we have identified glyceric acid (as calcium D-glycerate) and glyoxylic acid (as strontium oxalate after further oxidation to oxalic acid with bromine water), but insufficient lactic acid was recovered (as its zinc salt) for identification. The most significant fact, however, was the isolation of an acid, as its brucine salt, m. p. 210—212, $[\alpha]_D^{16}$ −31°. The brucine salts of D-threonic and D-erythronic acids have very similar properties, m. p. 212°, $[\alpha]_D^{20}$ −29·4° (Isbell, *J. Res. Nat. Bur. Stand.*, 1942, **29**, 227) and m. p. 212°, $[\alpha]_D^{20}$ −23° (Glattfield, *J. Amer. Chem. Soc.*, 1928, **50**, 149), respectively, and although the properties of our isolated product do not




(V)

exclude its identification as the salt of erythronic acid, they lie somewhat closer to those of threonic acid and thus support the probable structure for solanine and solasonine based on (III). It does, however, definitely exclude a structure based on 1 : 2-linkages as in (I) and (II).

As a further contribution to the relation of configuration to the rate of periodate oxidation we have oxidised amygdalin and rutin.

Amygdalin (V), which has its two glucose portions linked in the 1 : 1- and 6-positions (Campbell and Haworth, *J.*, 1924, 1337) was oxidised with periodate by Courtois and

Valentino (*Bull. Soc. Chim. biol.*, 1944, **26**, 469) and Halsall, Hirst, and Jones (*J.*, 1947, 1431). The former found that 2 mols. of formic acid were produced and 4 mols. of periodate consumed, the latter that 2 mols. of formic acid were produced, both results agreeing with the predicted values. We have confirmed these results in carrying out the experiment quantitatively at 25° (Fig. 2). The results differ, however, from those with solanine and solasodine. There is no rapid initial consumption of periodate or production of formic acid, which harmonises with the fact that amygdalin, unlike solanine and solasonine, contains no *cis*-groups. The action of periodate is thus similar to that of lead tetra-acetate in its action on triols (cf. Hockett, Dienes, and Ramsden, *loc. cit.*).

Rutin, a rhamnoglucoside of quercetin (Zemplén and Gerecs, *Ber.*, 1935, **68**, 1318), has its sugar moiety linked in the 1 : 1′- and 6′-positions respectively. Periodate oxidation of this compound with both a *cis-trans*- and a *trans-trans*-triol would have provided further useful information on the rates of reaction, simulating better the structures of solanine and solasonine. Preliminary experiments showed, however, that the consumption of periodate and production of formic acid went far beyond the expected 4 and 2 mols. respectively. It appears that the flavonol nucleus also underwent oxidation. Pennington and Ritter (*J. Amer. Chem. Soc.*, 1947, **69**, 187) observed the same behaviour with other substituted phenols.

Morindin, a rhamnoglucoside of morindone (1 : 5 : 6-trihydroxy-2-methylanthraquinone; Briggs and Dacre, *J.*, 1948, 564) could also provide additional evidence, but again preliminary investigations showed that 1-hydroxyanthraquinone could be oxidised by periodate to 1 : 4-dihydroxyanthraquinone and other yet unidentified products in small yield. Quercetin 3 : 7 : 3′ : 4′-tetramethyl ether, however, was not attacked by periodate.

## Experimental

Preliminary experiments were made to determine titratable formic acid in the presence of the aglycones, solanidine and solasodine, and the approximate quantity of periodate consumed and the formic acid produced in the oxidation of both solanine and solasonine before making quantitative measurements at 25°.

*Determination of Formic Acid consumed by Solanine and Solasonine.*—Formic acid (50 c.c. of 0·0075N) was added to two weighed samples of dried solasonine [(*a*) 0·2069, (*b*) 0·2055 g.], and each solution made up to 100 c.c. When dissolution was complete, 10-c.c. aliquots were removed and the amount of formic acid was determined by the addition of potassium iodide and estimation of the liberated iodine with 0·01N-sodium thiosulphate. Formic acid consumed per mol. of solasonine was (*a*) 0·981 and (*b*) 0·993 mol.

Similarly, solanine (0·0764 g.) was dissolved in formic acid (15 c.c. of 0·0112N), the solution made up to 100 c.c., and the amount of free formic acid in 25-c.c. aliquots determined. Formic acid consumed per mol. of solanine, 0·982 mol.

*Rate of Oxidation of Solanine by Sodium Metaperiodate at* 25°.—Finely powdered, dried solanine (0·3865 g.) was dissolved in formic acid [50 c.c.; 0·0112N (1·36 mols.)] and distilled water (100 c.c.). Sodium metaperiodate solution [70 c.c.; 0·305N (6·49 mols.) (Hill, *J. Amer. Chem. Soc.*, 1928, **50**, 2678), standardised by adding potassium iodide and sulphuric acid and titrating the liberated iodine with sodium thiosulphate solution] was added and the whole diluted to 500 c.c., shaken, and placed in a thermostat at 25°. All the reactants had been previously kept at 25° for ½ hr. Aliquot portions were removed at selected intervals (based on the preliminary experiments), and the periodate consumed and formic acid produced were determined as follows.

For the determination of periodate the reaction was stopped in aliquot samples (10 c.c.) by adding 20% potassium iodide solution (2 c.c.) and 2N-sulphuric acid (10 c.c.), and the liberated iodine titrated with 0·01N-sodium thiosulphate (starch). Since periodate liberates 4 mols. of iodine from acidified potassium iodide while iodate liberates only 3 mols., any difference in titre can be used to calculate the amount of periodate consumed.

For the determination of formic acid aliquot portions (25 c.c.) were removed and the oxidation stopped by adding excess (1 c.c.) of ethylene glycol, purified by distillation from solid potassium hydroxide and neutral to methyl-red. After 5 min., 1 c.c. of 20% potassium iodide solution was added and, after a further 5 min., the liberated iodine was titrated against 0·01N-sodium thiosulphate (starch). The results are illustrated in Fig. 1.

*Rate of Oxidation of Solasonine by Sodium Metaperiodate at 25°.*—Finely powdered dried solasonine (0·4300 g.) was dissolved in 0·0112N-formic acid (50 c.c., 1·25 mols.) and distilled water (100 c.c.). 0·305N-Sodium metaperiodate (70 c.c., 5·93 mols.) was added and the volume made up to 500 c.c. The above procedure was again followed with the results also illustrated in Fig. 1.

*Degradation of the Sugar Moiety of Solasonine to Simple Acids.*—Solasonine (4 g., 1 mol.) was added to a solution of sodium metaperiodate (5·4 g., 6 mols.) in water (400 c.c.) and the mixture set aside. The solasonine had dissolved completely within 5 hr. At the end of 3 weeks the solution became brown owing to the separation of inorganic material (350 mg.) which was filtered off. The colourless filtrate was acidified with 90% formic acid (1·2 g., 5·5 mols.), titrated with hot 10% strontium hydroxide solution (14 c.c.) (methyl-red), and set aside for several days at 0°. The white crystalline precipitate (5·1 g.), presumably a mixture of strontium periodate and iodate, was then filtered off. Concentrated hydrobromic acid (1 c.c.) was added and then bromine (9·5 g., 13 mols.), dropwise. Decolorisation occurred at first with evolution of gas and, on shaking, a curdy orange precipitate separated. The rotation of the solution became constant after 5 days, whereafter excess of bromine was removed by aeration for 10 hr. Hydrolysis was then brought about by heating at 100° for 20 hr., most of the precipitate dissolving. The remaining black residue (300 mg.) was removed and bromine (2 g., 3·1 mols.) again added to oxidise the expected glyoxylic acid to oxalic acid. A pale orange precipitate was again formed and after 2 days excess of bromine was removed as before. A black tar was filtered off. The clear solution was neutralised until alkaline to methyl-red but still just acid to phenolphthalein by the addition of solid strontium hydroxide (5 g.) and finally titration with hot 10% strontium hydroxide solution (13 c.c.). After several hours at 0° the pale brown precipitate was filtered off (fraction A; 900 mg.).

A sample of fraction A in hydrochloric acid gave an alkaloid test with Dragendorff's reagent. The whole fraction was therefore warmed with alcohol (50 c.c.), and the colourless residue (200 mg.) filtered off. This was dissolved in hot dilute hydrochloric acid and treated with dilute sulphuric acid until no more strontium sulphate was precipitated. The solution was then concentrated to a small volume. Colourless needles of oxalic acid dihydrate (100 mg.) separated, having m. p. and mixed m. p. 102°.

The filtrate from fraction A was freed from strontium ions by adding dilute sulphuric acid until precipitation was just complete, and filtering. After concentration in a vacuum to *ca.* 50 c.c. the filtrate was neutralised to methyl-red with zinc oxide (*ca.* 4 g.), and a dark brown residue filtered off from the hot solution. No zinc lactate could be detected in this residue which was almost completely soluble in alcohol. The solution remained clear on cooling, so it was again acidified with hydrobromic acid, concentrated to half-volume, and neutralised with zinc oxide. Brown resin was removed from the hot solution and on cooling to 0° a grey amorphous precipitate was removed (fraction B; 290 mg.).

Fraction B could not be completely redissolved in 5 c.c. of hot water. The insoluble portion was filtered off and the filtrate concentrated to a small volume. The colourless needles which separated (21 mg.) had $[\alpha]_D^{16}$ −4·9° [$l$ = 1 (micro-tube); $c$ 2·1 in $H_2O$) and were perhaps zinc lactate (Maclay, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1939, **61**, 1660, record $[\alpha]_D^{20}$ −7·7° for zinc L-lactate) but attempts to confirm this by the preparation of brucine lactate were unsuccessful.

The filtrate from fraction B was freed from zinc ions by the passage of hydrogen sulphide at a pH kept above 3 by the addition of sodium hydroxide solution, and separation of the zinc sulphide. Tests with Dragendorff's reagent at this stage still indicated the presence of alkaloid. Calcium bromide (5 g.) was added and then all bromide ions were removed by adding excess of silver sulphate solution and filtering. Sulphate ions were next removed by a sufficiency (no excess) of hot barium hydroxide solution, and silver ions by hydrogen sulphide. Excess of hydrogen sulphide was removed by aeration for 3 hr., and the solution concentrated in a vacuum to *ca.* 20 c.c. and just neutralised to phenolphthalein with calcium oxide. After the addition of alcohol (100 c.c.) a colourless amorphous precipitate was filtered off (fraction C; 300 mg.) and dissolved in hot water and the solution concentrated. Colourless needles separated on cooling (fraction D; 50 mg.), and after two recrystallisations from water had m. p. 138°, $[\alpha]_D^{16}$ +14·8° [$l$ = 1 (micro-tube); $c$ 3·1 in $H_2O$]. Jackson and Hudson (*J. Org. Chem.*, 1946, **11**, 614) record m. p. *ca.* 142°, $[\alpha]_D^{20}$ +15·5°, for calcium D-glycerate dihydrate.

The filtrate from fraction C was taken to dryness in a vacuum, yielding a white powder (150 mg.). This was dissolved in water (2 c.c.), dilute oxalic acid solution added until precipitation was complete, and the calcium oxalate filtered off. Alcohol (5 c.c.) and brucine

(0·8 g., 4 mols.) were added to the filtrate, and the mixture was heated at 100° for 3 hr. Excess of brucine was then removed with chloroform, and the solution concentrated in a vacuum to a thick syrup. This was finally dissolved in hot alcohol (2 c.c.) and allowed to crystallise. The colourless needles which separated (12 mg.), after repeated crystallisation from alcohol, had m. p. 210—212°, $[\alpha]_D^{16}$ −31° [$l$ = 1 (micro-tube); $c$ 1 in $H_2O$]. Isbell (*J. Res. Nat. Bur. Stand.*, 1942, **29**, 227) records m. p. 212°, $[\alpha]_D^{20}$ −29·4°, for brucine D-threonate.

*Rate of Oxidation of Amygdalin by Sodium Metaperiodate at* 25°.—Amygdalin (0·1803 g.) was dissolved in water (100 c.c.), 0·305N-sodium metaperiodate (50 c.c.) added, and the mixture made up to 500 c.c., shaken well, and placed in a thermostat at 25°. The reactants had previously been kept at 25° for ½ hr. The periodate and formic acid were determined at intervals, selected from preliminary experiments; results are recorded graphically in Fig. 2.

*Oxidation of* 1-*Hydroxyanthraquinone with Sodium Metaperiodate.*—In a preliminary experiment 1-hydroxyanthraquinone (0·0314 g.; purified by chromatography on freshly calcined magnesia) was dissolved in an aqueous solution of sodium hydroxide (0·5 g. in 300 c.c.), 0·308N-sodium metaperiodate [(15 c.c., 4·25 mols.) added, and the mixture made up to 500 c.c. The amount of periodate consumed was determined at intervals in the usual way [Found: periodate per mol. of 1-hydroxyanthraquinone: 1·1 (1 hr.), 1·76 (2 hr.), 2·19 (3 hr.), 3·88 (14·5 hr.), 4·25 mols. (26·5 hr.)].

In an experiment to isolate the oxidation products chromatographically, pure 1-hydroxyanthraquinone (1 g.) in sodium hydroxide solution (5 g. in 2 l.) was allowed to react with sodium metaperiodate solution (1 g. in 50 c.c.; 1 mol.) for 3 days. In this time a dark brown solid had precipitated which was filtered off, acidified with dilute hydrochloric acid, dried (yield, 210 mg.), dissolved in acetone, and chromatographed on magnesia. The main solution was acidified and set aside for some days. A similar precipitate formed which was also treated as above (yield, 1·1 g.). The chromatograms and the colour of the products obtained from similar bands appeared identical in each case, so the products were combined. Systematic chromatography of the material and development of the bands with acetone and acetone containing acetic acid (cf. Briggs and Nicholls, *J.*, 1949, 1241) afforded five major bands: dark blue, brown, mauve, red, and salmon. The distinct bands were decomposed with dilute hydrochloric acid, and the liberated anthraquinones filtered off. The respective products were brown (5 mg.), orange (85 mg.), orange-red (17 mg.), yellow (530 mg.), and yellow (250 mg.).

Despite the distinct difference in colour of the final two bands the material recovered from each proved to be unchanged 1-hydroxyanthraquinone (yellow needles, m. p. and mixed m. p. 196—196·5°, after crystallisation from alcohol).

The material from the mauve band was purified by sublimation at 120—150°/0·05 mm. The m. p. of the product, 188°, was not depressed by an authentic specimen of 1 : 4-dihydroxyanthraquinone while its colour reactions and its half-wave potential (−0·788 v) were also identical.

Unfortunately most of the material from the brown band was lost and there was insufficient material from this and the first dark blue band for identification.

We are indebted to the Chemical Society and the Royal Society of New Zealand for continued grants, to Imperial Chemical Industries Limited, Dyestuffs Division, and S. B. Penick and Company for gifts of chemicals, and one of us (L. C. V.) for a Returned Serviceman's Senior, Scholarship.

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# 567. *Quinoxaline N-Oxides. Part I. The Oxidation of Quinoxaline and its Bz-Substituted Derivatives.*

By Justus K. Landquist.

Quinoxaline and its *Bz*-alkyl, -alkoxy-, -halogeno-, and acylamino-derivatives are oxidised to mono- and di-*N*-oxides by organic peracids. Negative substituents promote the simultaneous formation of 2 : 3-dihydroxyquinoxaline derivatives. Resistance to *N*-oxidation, due to steric or polar influences, is encountered in 5- and 8-substituted quinoxalines. The reactions of some *N*-oxides with methyl iodide and with phosphoryl chloride are examined.

Quinoxaline 1 : 4-dioxide (I) and its 2-methyl-, 3-*n*-amyl-2-methyl-, and 2 : 3-tetramethylene derivatives were prepared by McIlwain (*J.*, 1943, 322) as possible antagonists of the *K* vitamins and related compounds and they have been shown to have moderate antibacterial activity *in vitro* (McIlwain, *loc. cit.*; Wiedling, *Acta Path. Microbiol. Scand.*, 1945, **22**, 379; Frisk, *Acta Med. Scand.*, 1946, **125**, 487; Iland, *Nature*, 1948, **161**, 1010). Some hydroxy- and methoxy-derivatives were synthesised by King, Clark, and Davis (*J.*, 1949, 3012) as possible antibacterials related to iodinin, and (I) and its 2-methyl-, 2-sulphanilamido-, and 2 : 3-diphenyl derivatives have been tested as antimalarials (Wiselogle, "Survey of Antimalarial Drugs, 1941—1945," Edwards, Ann Arbor, Mich., 1946, Vol. II, p. 1472) with negative results. During an investigation of quinoxaline derivatives as amœbicides it was found in these laboratories that 2-methylquinoxaline 1 : 4-dioxide was highly active against amœbiasis in rats, and this prompted a re-examination of this field from both the chemical and the biological standpoint. The preparation of some quinoline and quinoxaline *N*-oxides for examination as amœbicides was subsequently reported by Mamalis and Petrow (*J.*, 1950, 703) but no details were given.

Quinoxaline *N*-oxides have been made hitherto by oxidation with hydrogen peroxide in acetic acid. It is advantageous to use the 1·2M-solution of peracetic acid obtained by treating 30% hydrogen peroxide with acetic anhydride and sulphuric acid, the latter being neutralised by the subsequent addition of sodium acetate (Byers and Hickinbottom, *J.*, 1948, 286). Performic acid and concentrated peracetic acid (6·5 or 10M) are more potent but less controllable reagents. Hydrogen peroxide alone, or with sulphuric acid or phosphoric acid, oxidises quinoxaline to quinoxaline 1-oxide (II) together with much tar and insoluble, high-melting by-products, but organic peracids oxidise quinoxaline cleanly to either (I) or (II) according to the conditions.

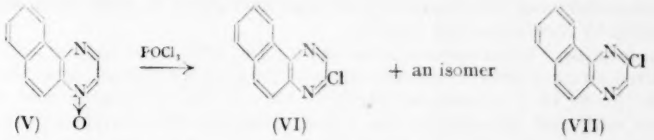
(I) (II) (III) (IV)

5-Substituted quinoxalines afford mono-*N*-oxides which are considered to be the 1-oxides, but with the exception of the 5-methoxy-compound they are highly resistant to further oxidation to di-*N*-oxides. This is attributable to steric hindrance (which is least with the methoxyl group) and to the reduced electron density at the tertiary nitrogen atom in the mono-*N*-oxides. No *N*-oxide is obtained from 5 : 8-dichloroquinoxaline, but 5 : 6 : 7 : 8-dibenzoquinoxaline (phenanthrapyrazine) gives a mono-*N*-oxide. Both mono- and di-*N*-oxides are obtained from 6- and 7-substituted quinoxalines, but 6-halogeno-compounds give mainly mono-*N*-oxides unless fairly drastic oxidation conditions (*e.g.*, performic acid) are used. Quinoxalines unsubstituted in the heterocyclic nucleus undergo simultaneous oxidation to 2 : 3-dihydroxy-derivatives; with 6-methylquinoxaline this is negligible (*ca.* 1%), but negative substituents favour the reaction, 6-halogenoquinoxalines

giving about 30% of the 2 : 3-dihydroxy-compounds while 6-nitro- and 6-cyano-quinoxaline give 50—60% with only traces of *N*-oxides. 2 : 3-Dihydroxyquinoxalines are conveniently characterised by boiling them with phosphoryl chloride and dimethylaniline, to give the 2 : 3-dichloro-derivatives; methylation to give 1 : 2 : 3 : 4-tetrahydro-1 : 4-dimethyl-2 : 3-dioxoquinoxalines is not always satisfactory, 6-cyano-2 : 3-dihydroxy- and 2 : 3-dihydroxy-6-nitroquinoxaline, for example, giving monomethyl derivatives. Peracetic acid oxidation of 6-iodoquinoxaline and of 6 : 7-benzoquinoxaline is abnormal, possibly involving attack at the *meso*-positions in the latter case. 2 : 3-Dichloroquinoxaline is resistant to oxidation by peracetic acid, but 2-chloroquinoxaline is oxidised to a mono-*N*-oxide, which is regarded as 2-chloroquinoxaline 4-oxide.

With the foregoing exceptions quinoxaline mono-*N*-oxides are readily oxidised to di-*N*-oxides from which they are distinguished by lower melting points and greater solubility in non-polar solvents. Methyl iodide reacts with (II), but not with 5 : 6-benzoquinoxaline 1-oxide (V), to give a quaternary derivative. Of the alternative structures, 1-methylquinoxalinium 4-oxide iodide (III) and methoxyquinoxalinium iodide (IV), the former is preferred as the substance does not yield formaldehyde or quinoxaline on alkaline degradation. The yellow aqueous solution of (III) becomes deep blue-green on addition of sodium hydroxide, the colour fading on heating

Phosphoryl chloride reacts vigorously with (I) and (II), giving 2 : 3-dichloro- and 2-chloro-quinoxaline respectively. 5-Methylquinoxaline 1-oxide is converted into 2-chloro-5-methylquinoxaline, but two isomeric chlorobenzoquinoxalines are obtained from (V). Neither of these is identical with 3-chloro-5 : 6-benzoquinoxaline (VII), which was made by an unambiguous route from 2-carbethoxymethylaminonaphthalene. One of the isomers




(V) (VI) (VII)

was identified as 2-chloro-5 : 6-benzoquinoxaline (VI) by its reactivity with boiling piperidine, the other isomer being unaffected by this reagent. The unreactive isomer was not obtained by direct chlorination of 5 : 6-benzoquinoxaline in acetic acid, the product being a dichlorobenzoquinoxaline which also was unaffected by boiling piperidine.

## Experimental

*o-Phenylenediamines.*—*3-Ethoxy-o-phenylenediamine.* 2 : 3-Dinitrophenetole (80 g.) dissolved in methanol (600 c.c.) was hydrogenated over Raney nickel at room temperature. Evaporation of the filtered solution under reduced pressure gave a dark oil (54 g.) which was used without further purification. The diamine formed a *picrate*, yellow needles (from ethanol), m. p. 210—212° (Found: C, 44·15; H, 4·0; N, 18·5. $C_8H_{12}ON_2,C_6H_3O_7N_3$ requires C, 44·1; H, 3·9; N, 18·4%).

4 : 5-*Diamino-2-bromotoluene.* (*a*) 2-Bromo-4-nitrotoluene (108 g.) was added during 45 min. to a mixture of sulphuric acid (465 c.c.; *d* 1·84) and nitric acid (150 c.c.; *d* 1·4) at 40—45°, and the mixture was heated at 90° for 2·25 hr., cooled, and poured on ice (3 kg.). The solid product was crystallised from ethanol, to give *2-bromo-4 : 5-dinitrotoluene* (55 g. of m. p. 92—94°), colourless leaflets, m. p. 94—95° (Found: N, 10·4. $C_7H_5O_4N_2Br$ requires N, 10·7%). This compound (108 g.), heated with ethanolic ammonia (600 c.c.; saturated at 0°) for 5 hr. at 120° (340 lb./sq. in.), gave 65 g. of mixed bromonitrotoluidines, m. p. 164—166°, which on reduction with zinc dust and sodium hydroxide in ethanol afforded *4 : 5-diamino-2-bromotoluene*, faintly brown leaflets (from light petroleum), m. p. 140—141° (Found: N, 14·0. $C_7H_9N_2Br$ requires N, 13·9%). (*b*) 4-Acetamido-2-bromotoluene was nitrated and the product hydrolysed to 4-amino-2-bromo-5-nitrotoluene, m. p. 163—164°, which was reduced similarly to the diamine.

*Quinoxalines.*—The following general method of preparation was employed: glyoxal sodium bisulphite (0·25 mole), an *o*-phenylenediamine (0·25 mole), and water (300 c.c.) were stirred at 60° for 3 hr., more glyoxal sodium bisulphite (10% of the original charge) being added after 1 hr. The mixture was then made strongly alkaline with potassium hydroxide, and the

quinoxaline was isolated by filtration, steam-distillation, or extraction with ether. The following quinoxalines (colourless except as stated) were made by this method :

5-*Methylquinoxaline*, pale yellow, m. p. 20—21°, b. p. 120°/15 mm. (Found : N, 19·5. $C_9H_8N_2$ requires N, 19·45%), changing in moist air to a *hydrate*, m. p. 49—50° (Found : N, 17·1. $C_9H_8N_2,H_2O$ requires N, 17·3%).

5-*Ethoxyquinoxaline*, rhombs, m. p. 63—64°, b. p. 165—166°/18 mm. (Found : N, 16·2. $C_{10}H_{10}ON_2$ requires N, 16·1%).

5-*Chloroquinoxaline*, cream needles [from light petroleum (b. p. 40—60°)], m. p. 60—62° (Found : N, 17·3. $C_8H_5N_2Cl$ requires N, 17·0%).

6-*Iodoquinoxaline*, m. p. 114—115° (from benzene), steam-volatile (Found : N, 10·7. $C_8H_5N_2I$ requires N, 10·9%).

6-*Cyanoquinoxaline*, needles (from ethanol), m. p. 176—178° (Found : N, 26·6. $C_9H_5N_3$ requires N, 27·1%).

6 : 7-*Dimethylquinoxaline*, plates [from light petroleum (b. p. 80—100°)], m. p. 100—101° (Found : N, 17·7. $C_{10}H_{10}N_2$ requires N, 17·7%).

6 : 7-*Benzoquinoxaline*, needles [from light petroleum (b. p. 60—80°)], m. p. 125—126°, steam-volatile (Found : N, 15·55. $C_{12}H_8N_2$ requires N, 15·55%).

6-*Chloro*-7-*methylquinoxaline*, needles [from light petroleum (b. p. 100—120°)], m. p. 120—122° (Found : N, 15·8. $C_9H_7N_2Cl$ requires N, 15·7%).

6-*Bromo*-7-*methylquinoxaline*, needles [from light petroleum (b. p. 100—120°)], m. p. 127—128° (Found : N, 12·2. $C_9H_7N_2Br$ requires N, 12·55%).

6 : 7-*Dichloroquinoxaline*, laminæ [from light petroleum (b. p. 100—120°)], m. p. 210° (Found : C, 48·3; H, 2·0; N, 14·2. $C_8H_4N_2Cl_2$ requires C, 48·2; H, 2·0; N, 14·1%).

5 : 8-*Dichloroquinoxaline*, needles [from light petroleum (b. p. 100—120°)], m. p. 205—207° (Found : N, 13·9%).

5-Chloroquinoxaline and 6-iodoquinoxaline were also made in poor yield from 5- and 6-aminoquinoxaline by the Sandmeyer reaction.

6-*Bromoquinoxaline*. 6-Aminoquinoxaline (14·5 g.) in 10% hydrobromic acid (60 c.c.) was added to a stirred mixture of 48% hydrobromic acid (40 c.c.), ice (200 g.), and saturated sodium nitrite solution (from 10 g. of sodium nitrite). After 5 min. sulphamic acid was added to destroy nitrous acid, and the solution was added to an ice-cold solution of cuprous bromide (17 g.) in 48% hydrobromic acid (50 c.c.). After 16 hr. the mixture was heated at 100° for 1 hr. made alkaline, and steam-distilled. 6-*Bromoquinoxaline* (5·6 g.) was isolated from the distillate by extraction with benzene and distillation, and had b. p. 146—149°/18 mm., f. p. 48—49° (Found : N, 13·5. $C_8H_5N_2Br$ requires N, 13·4%).

6-*Acetamidoquinoxaline* (first made in these laboratories by Dr. A. F. Crowther). 6-Aminoquinoxaline (Hinsberg, *Annalen*, 1887, **237**, 345) (15 g.), acetic anhydride (13·5 c.c.), and benzene (200 c.c.) were boiled under reflux for 1·5 hr., and the *product* (18·1 g.; m. p. 196°) was collected when cold. It formed pale cream needles, m. p. 196·5°, from water (Found : C, 64·05; H, 5·05; N, 22·55. $C_{10}H_9ON_3$ requires C, 64·2; H, 4·7; N, 22·5%). 5-Acetamidoquinoxaline was made similarly from 5-aminoquinoxaline (Jensen, *Acta Chem. Scand.*, 1948, **2**, 91).

N-6-*Quinoxalylsuccinamic acid*. 6-Aminoquinoxaline (12·6 g.), succinic anhydride (8·7 g.), and dry toluene (400 c.c.) were boiled under reflux for 10 min., then cooled, and the toluene was decanted. The solid residue was extracted with 10% sodium carbonate solution (100 c.c.) and the filtered extract was acidified with hydrochloric acid. The *product* separated slowly as a red-brown solid [9·7 g.; m. p. 216—217° (decomp.)] which gave light brown crystals, m. p. 217°, from glacial acetic acid (Found : C, 58·5; H, 4·5; N, 17·2. $C_{12}H_{11}O_3N_3$ requires C, 58·8; H, 4·5; N, 17·1%).

N-*Oxides*.—*Quinoxaline* 1-*oxide*. Quinoxaline (32·5 g., 0·25 mole) and 1·2M-peracetic acid (210 c.c., 0·25 mole) were heated overnight at 50°, and the mixture was poured on ice (600 g.), neutralised with 40% sodium hydroxide solution, and extracted with chloroform. The dried ($Na_2SO_4$) extract was evaporated and the residue crystallised from *cyclo*hexane, giving *quinoxaline* 1-*oxide* (II) as colourless needles (20 g.), m. p. 122—123° (Found : C, 66·1; H, 4·1; N, 19·4. $C_8H_6ON_2$ requires C, 65·75; H, 4·1; N, 19·2%).

*Quinoxaline* 1 : 4-*dioxide* (I). Quinoxaline (50 g.) and 1·2M-peracetic acid (1 l.) were heated overnight at 50°, a slightly exothermic reaction being observed at first. The mixture was evaporated at 10—15 mm. on the water-bath to about 200 c.c., poured on ice (500 g.), and neutralised with 40% aqueous sodium hydroxide, care being taken to avoid excess of this reagent. The precipitate (40—50 g.) was collected and washed with water, and the mother-liquor was extracted with chloroform to recover a further 9 g. of crude quinoxaline 1 : 4-dioxide.

Two crystallisations from ethanol gave golden-yellow needles (30—39 g.), m. p. 241—243° (Found: C, 59·2; H, 4·0; N, 17·3. Calc. for $C_8H_6O_2N_2$: C, 52·25; H, 3·7; N, 17·3%). (Note: the m. p.s of quinoxaline dioxides are greatly depressed if the samples are heated slowly, or are kept for any length of time at an elevated temperature.)

*Oxidation of 5-methylquinoxaline.* (*a*) 5-Methylquinoxaline (7·2 g.) and 1·2M-peracetic acid (200 c.c.) were heated overnight at 50°, diluted with ice (300 g.), and neutralised with 40% aqueous sodium hydroxide. The precipitated *5-methylquinoxaline 1-oxide* (4·6 g.) was collected, extraction of the mother-liquor with chloroform yielding a further 1·7 g.; it crystallised from light petroleum (b. p. 100—120°) in colourless needles of the *hydrate*, becoming reddish-orange on exposure to light (see Table 1). (*b*) 5-Methylquinoxaline (7·2 g.) and concentrated peracetic acid (20 c.c. of 10M or 30 c.c. of 6·5M) were heated to 50° and then cooled in ice to control the violent exothermic reaction. The mixture was then heated overnight at 50°, cooled, neutralised with 40% aqueous sodium hydroxide and ice, and filtered from 5-methylquinoxaline 1-oxide (2·7 g.). The filtrate was extracted with chloroform, and the dried ($Na_2SO_4$) extract evaporated. The residue was extracted with boiling *cyclo*hexane to remove monoxide (0·5 g.), and the undissolved *5-methylquinoxaline 1 : 4-dioxide* (0·2 g.) was crystallised from ethanol (see Table 1).

TABLE 1. *N-Oxides of substituted quinoxalines.*

| Substituent | Degree of oxidation | Formula | M. p. | Found, % C | Found, % H | Found, % N | Required, % C | Required, % H | Required, % N |
|---|---|---|---|---|---|---|---|---|---|
| 5-Me | Mono | $C_9H_8ON_2,H_2O$ | 131—132° | — | — | 15·7 [a] | — | — | 15·7 |
| | Di | $C_9H_8O_2N_2$ | 192—194 | 61·1 | 4·5 | 15·6 | 61·36 | 4·55 | 15·9 |
| 6-Me | Di | $C_9H_8O_2N_2$ | 218—219 | 61·4 | 4·5 | 15·7 | 61·36 | 4·55 | 15·9 |
| 6 : 7-$Me_2$ | Di | $C_{10}H_{10}O_2N_2$ | 220 | 63·0 | 5·4 | 14·7 | 63·16 | 5·25 | 14·7 |
| 5 : 6-Benzo | Mono | $C_{12}H_8ON_2$ | 158—159 | — | — | 14·8 | — | — | 14·3 |
| | Di | $C_{12}H_8O_2N_2$ | 215—216 | 67·8 | 4·0 | 13·0 | 67·9 | 3·8 | 13·2 |
| 5 : 6-7 : 8-Dibenzo | Mono | $C_{14}H_{10}ON_2$ | 243—244 | 77·1 | 4·1 | 10·7 | 78·0 | 4·05 | 11·4 |
| 5-MeO | Di | $C_9H_8O_3N_2$ | 222 | 56·5 | 4·4 | 14·8 | 56·2 | 4·2 | 14·6 |
| 5-EtO | Mono | $C_{10}H_{10}O_2N_2$ | 114—116 | 63·1 | 5·3 | 14·5 | 63·16 | 5·25 | 14·7 |
| 6-MeO | Di | $C_9H_8O_3N_2$ | 227—228 [b] | 56·2 | 4·3 | 15·3 | 56·2 | 4·2 | 14·6 |
| 6-EtO | Di | $C_{10}H_{10}O_3N_2$ | 192—194 | 57·6 | 4·95 | 13·75 | 58·25 | 4·85 | 13·6 |
| 5 : 6-$(MeO)_2$ | Mono | $C_{10}H_{10}O_3N_2$ | 138—140 | 57·95 | 5·0 | 13·8 | 58·25 | 4·85 | 13·6 |
| | Di | $C_{10}H_{10}O_4N_2$ | 220—222 | 53·8 | 4·8 | 12·55 | 54·0 | 4·5 | 12·6 |
| 6 : 7-$(MeO)_2$ | Di | $C_{10}H_{10}O_4N_2$ | 264—265 [c] | 55·0 | 4·6 | 12·5 | 54·0 | 4·5 | 12·6 |
| 2-Cl | Mono | $C_8H_5ON_2Cl$ | 150—152 | 53·1 | 3·0 | 15·7 | 53·2 | 2·8 | 15·5 |
| 5-Cl | Mono | $C_8H_5ON_2Cl$ | 177—179 | 51·7 | 2·7 | 15·4 | 53·2 | 2·8 | 15·5 |
| 6-Cl | Mono | $C_8H_5ON_2Cl$ | 151—152 | 53·5 | 2·8 | 15·2 | 53·2 | 2·8 | 15·5 |
| | Di | $C_8H_5O_2N_2Cl$ | 211—212 | 49·5 | 2·5 | 14·0 | 48·85 | 2·5 | 14·3 |
| 6-Br | Di | $C_8H_5O_2N_2Br$ | 223—225 | 39·7 | 2·0 | 11·7 | 39·9 | 2·1 | 11·6 |
| 6 : 7-$Cl_2$ | Di | $C_8H_4O_2N_2Cl_2$ | 206—208 | 42·1 | 1·7 | 12·7 | 41·55 | 1·7 | 12·1 |
| 6-Cl-7-Me | Mono | $C_9H_7ON_2Cl$ | 166—168 | — | — | 14·1 | — | — | 14·4 |
| | Di | $C_9H_7O_2N_2Cl$ | 227 | 51·45 | 3·45 | 13·0 | 51·3 | 3·3 | 13·3 |
| 6-Br-7-Me | Mono | $C_9H_7ON_2Br$ | 167—168 | 45·25 | 2·95 | 11·6 | 45·2 | 2·9 | 11·7 |
| | Di | $C_9H_7O_2N_2Br$ | 222—224 | 42·35 | 3·0 | 10·45 | 42·3 | 2·75 | 11·0 |
| 5-NHAc | Mono | $C_{10}H_9O_2N_3$ | 175—178 | 59·0 | 4·6 | 20·3 | 59·1 | 4·4 | 20·7 |
| | Di? | — | 230—232 | Insufficient for analysis | | | | | |
| 6-NHAc | Di | $C_{10}H_9O_2N_3$ | 245—247 | 54·8 | 4·2 | 18·9 | 54·8 | 4·1 | 19·2 |
| [d] | Di | $C_{12}H_{11}O_5N_3$ | 242—244 | 52·1 | 3·9 | 14·8 | 52·0 | 4·0 | 15·2 |

[a] Loss at 100°/0·05 mm., 10%. $1H_2O$ requires 10·1%. [b] Lit., m. p. 207—210° (decomp.). [c] Lit., decomp. at *ca.* 250°. [d] Substituent, 6-$HO_2C{\cdot}[CH_2]_2{\cdot}CO{\cdot}NH$.

*Oxidation of 6-chloroquinoxaline.* (*a*) 6-Chloroquinoxaline (8·2 g.), glacial acetic acid (200 c.c.), and 30% hydrogen peroxide (50 c.c.) were heated at 50° overnight, cooled, and filtered from 6-chloro-2 : 3-dihydroxyquinoxaline (3 g.). The filtrate was neutralised with 40% aqueous sodium hydroxide and ice, and was extracted with chloroform. Evaporation of the dried ($Na_2SO_4$) extract gave crude *6-chloroquinoxaline mono-N-oxide* (1·1 g.; m. p. 115°) which was crystallised repeatedly from ethanol (see Table 1). (*b*) Crude 6-chloroquinoxaline mono-*N*-oxide (2·6 g.) and 1·2M-peracetic acid (20 c.c.) were heated at 50° overnight, poured on ice (100 g.), and neutralised with 40% sodium hydroxide solution. The precipitated *6-chloroquinoxaline 1 : 4-dioxide* was collected, washed with water, and crystallised from ethanol. (*c*) 6-Chloroquinoxaline (3·1 g.), anhydrous formic acid (60 c.c.) (or 32 c.c. of 85% formic acid and 26 c.c. of acetic anhydride) and 30% hydrogen peroxide (20 c.c.) were heated cautiously to 40—50°, and the vigorous exothermic reaction was controlled by cooling to prevent the temperature exceeding 60°. When the reaction abated the mixture was heated at 50° overnight, cooled, filtered from 6-chloro-2 : 3-dihydroxyquinoxaline (0·8 g.), and evaporated at 15—20 mm.

to about 20 c.c. Neutralisation with 40% aqueous sodium hydroxide and ice precipitated crude di-*N*-oxide (1·75 g.).

*Oxidation of* 5 : 6-*benzoquinoxaline.* (*a*) 5 : 6-Benzoquinoxaline (9 g.), anhydrous formic acid (150 c.c.), and 30% hydrogen peroxide (50 c.c.) were heated at 50° overnight (the initial exothermic reaction being controlled by cooling), poured into ice-water (500 c.c.), and filtered from 5 : 6-*benzoquinoxaline* 1-*oxide* (V), (8·9 g.). The filtrate was neutralised at 0—10° with 40% sodium hydroxide solution and extracted with chloroform. The dried extract was evaporated, the residue was extracted with boiling light petroleum (30 c.c.; b. p. 100—120°) to remove 5 : 6-benzoquinoxaline 1-oxide, and the undissolved 5 : 6-*benzoquinoxaline* 1 : 4-*dioxide* (0·15 g.) was crystallised from ethanol (see Table 1). (*b*) (V) (7·2 g.) and 1·2M-peracetic acid (60 c.c.) were heated at 60° for 96 hr., further additions of peracetic acid (16 c.c. each) being made after 24 and 48 hr., and the mixture was then concentrated under reduced pressure and neutralised (pH 7·0) with sodium hydroxide solution and ice. The precipitated solid (5·9 g.) was extracted with light petroleum (b. p. 100—120°) to remove (V), and the residue was crystallised from ethanol, giving 5 : 6-benzoquinoxaline 1 : 4-dioxide (0·45 g.).

Details of substituted quinoxaline *N*-oxides prepared by the foregoing methods are given in Table 1. In all cases the preparation of di-*N*-oxides was attempted, and mono-*N*-oxides were isolated only when they were obtained in such experiments. Table 2 gives the yields of crude 2 : 3-dihydroxyquinoxalines obtained as by-products in these oxidations; the 2 : 3-dichloro-derivatives were obtained by boiling the 2 : 3-dihydroxy-compounds (1 g.) with phosphoryl chloride (5 g.) and dimethylaniline (0·5—1 g.) for 0·5—4 hr., pouring on ice, and crystallising the solid from light petroleum.

1-*Methylquinoxalinium iodide* 4-*oxide.* (*a*) The oxide (II) (2 g.) and methyl iodide (4 c.c.) in acetonitrile (20 c.c.) were set aside in the dark. After 36 hr. the product (0·5 g.) was filtered off; the mother-liquors slowly deposited more (1·5 g.). The *iodide* crystallised from ethanol in brown laminæ, m. p. 188—189° (Found: C, 38·0; H, 3·5; N, 9·6; I, 43·2. $C_9H_9ON_2I$ requires C, 37·5; H, 3·1; N, 9·7; I, 44·1%). (*b*) The oxide (II) (1·5 g.) and methyl iodide (1·5 c.c.) were mixed in a stoppered vessel protected from light. The mixture became brown and after 1 month the product was crystallised twice from ethanol (yield 1·5 g.; m. p. 187—188°).

TABLE 2. *Oxidation of quinoxalines to* 2 : 3-*dihydroxy-derivatives by peracetic or performic acid.*

| Substituent | 2 : 3-Dihydroxy-compounds, approx. yield (%) | 2 : 3-Dichloroquinoxalines | | | |
|---|---|---|---|---|---|
| | | Formula | M. p. | N, found, % | N, reqd., % |
| 6-Me | 1 | $C_9H_6N_2Cl_2$ | 112° [a] | — | — |
| 5-Cl | 30 | $C_8H_3N_2Cl_3$ | 142—143 | 12·2 | 12·0 |
| 6-Cl | 15—30 | $C_8H_3N_2Cl_3$ | 144 [b] | — | — |
| 6-Br | 28 | $C_8H_3N_2Cl_2Br$ | 132 [c] | — | — |
| 5 : 8-$Cl_2$ | 65 | $C_8H_2N_2Cl_4$ | 160—161 | 10·7 | 10·45 |
| 6 : 7-$Cl_2$ | 43 | $C_8H_2N_2Cl_4$ | 170—170·5 | 10·0 | 10·45 |
| 6-Cl, 7-Me | 10 | $C_9H_5N_2Cl_3$ | 172—173 | 11·4 | 11·3 |
| 6-Br, 7-Me | 12—16 | $C_9H_5N_2Cl_2Br$ | 160—161 | 9·5 | 9·6 |
| 6-CN | 50 | — | — | — | — |
| 6-$NO_2$ | 60 | $C_8H_3O_2N_3Cl_2$ | 150 [d] | — | — |

Recorded m. p.s (*a*) 114°, (*b*) 143—144°, (*c*) 132°, (*d*) 152°.

*Reaction of Phosphoryl Chloride with Quinoxaline N-Oxides.*—(*a*) The oxide (II) (2 g.) was added cautiously to phosphoryl chloride (10 c.c.). The vigorous exothermic reaction was controlled by cooling, and the mixture was then boiled under reflux for 15 min., poured on crushed ice (150 g.), and made strongly alkaline with potassium hydroxide solution (cooling in ice). The product was extracted with ether, and the dried ($Na_2SO_4$) extract evaporated. The residue (2·1 g.), dissolved in light petroleum (b. p. 40—60°), was decolorised by passage through alumina, and the solution was concentrated to yield white needles, m. p. 46—48°, undepressed by admixture with authentic 2-chloroquinoxaline. Under the same conditions, (I) gave 2 : 3-dichloroquinoxaline, and 5-methylquinoxaline 1-oxide gave 2-chloro-5-methylquinoxaline, m. p. 95°, identical with a sample made from *N*-(6-nitro-*o*-tolyl)glycine (Me = 2) (Platt and Sharp, *J.*, 1948, 2129).

(*b*) The oxide (V) (7·2 g.) and phosphoryl chloride (35 c.c.) were boiled under reflux for 15 min., cooled, poured on ice (300 g.), and made alkaline with potassium hydroxide. The product was washed with water and dried at 40°. The solid (7·8 g.; m. p. 86—98°) was dissolved in 3 : 1 light petroleum (b. p. 60—80°)–benzene and chromatographed on alumina,

giving 2-*chloro*-5 : 6-*benzoquinoxaline* (4·4 g.), m. p. 120·5° (Found : C, 66·9; H, 3·3; N, 12·2. $C_{12}H_7N_2Cl$ requires C, 67·1; H, 3·25; N, 13·05%). Further elution of the alumina with 1 : 1 light petroleum–benzene gave a *chloro*-5 : 6-*benzoquinoxaline* (1·8 g.), m. p. 104—104·5° (Found : C, 67·1; H, 3·5; N, 12·3%).

2-*Chloro*-7 : 8-*benzoquinoxaline*. Ethyl 2-naphthylaminoacetate (7·7 g.), dissolved in ethanol (70 c.c.), was treated with a diazo-solution prepared from aniline (3·1 g.) in 2·5N-hydrochloric acid (30 c.c.) and sodium nitrite (2·4 g.) in water (7 c.c.), and then with sodium acetate trihydrate (1·6 g.). After 1 hour's stirring the product was collected, washed with 60% aqueous ethanol and with water, and crystallised from butanol, giving *ethyl* 1-*phenylazo*-2-*naphthylaminoacetate* (6·9 g.), red needles, m. p. 135—136° (Found : N, 12·1. $C_{20}H_{19}O_2N_3$ requires N, 12·6%). This compound (42 g.) in ethanol (500 c.c.) was hydrogenated over Raney nickel at 60°/50 atm., and evaporation of the resulting solution and extraction of the catalyst sludge with acetone gave 1 : 2 : 3 : 4-*tetrahydro*-2-*oxo*-7 : 8-*benzoquinoxaline* (20·5 g.), m. p. 197—198° (Found : C, 73·0; H, 5·2; N, 14·5. $C_{12}H_{10}ON_2$ requires C, 72·7; H, 5·05; N, 14·1%). This was dissolved in hot alkaline hydrogen peroxide (250 c.c. of 0·5N-sodium hydroxide and 60 c.c. of 6% hydrogen peroxide), and the solution was clarified with carbon, diluted to 500 c.c., and acidified with acetic acid, to precipitate 2-hydroxy-7 : 8-benzoquinoxaline (17·5 g.), which crystallised from dioxan as a *hydrate*, m. p. 275—275·5° (Found : C, 66·6; H, 4·2; N, 13·1. $C_{12}H_8ON_2,H_2O$ requires C, 67·3; H, 4·66; N, 13·1%). The hydroxy-compound (21 g.) and phosphoryl chloride (105 c.c.) were refluxed for 45 min. and poured on ice. The aqueous layer was decanted and the residue was treated with ice and potassium hydroxide solution until alkaline, filtered, and washed with water. Crystallisation of the dried solid from light petroleum (b. p. 80—100°) gave 2-*chloro*-7 : 8-*benzoquinoxaline* (15·1 g.) as pale yellow needles, m. p. 128—129° (Found : C, 67·3; H, 3·8; N, 12·1. $C_{12}H_7N_2Cl$ requires C, 67·1; H, 3·25; N, 13·05%).

1 : 2 : 3 : 4-*Tetrahydro*-5-*methyl*-2-*oxoquinoxaline*. *N*-(6-Nitro-*o*-tolyl)glycine (Me = 2) (4·6 g.) in ethanol (100 c.c.) was hydrogenated over Raney nickel at 60°/60 atm. Evaporation of the filtered solution and crystallisation from benzene gave the *product* (1·7 g.) as colourless needles, m. p. 177—180° (Found : C, 66·6; H, 6·3; N, 17·3. $C_9H_{10}ON_2$ requires C, 66·67; H, 6·16; N, 17·3%), which were readily oxidised to 2-hydroxy-5-methylquinoxaline, m. p. 282—283°.

2-*Piperidino*-7 : 8-*benzoquinoxaline*. 2-Chloro-7 : 8-benzoquinoxaline (1·5 g.) and piperidine (5 c.c.) were boiled under reflux for 1·5 hr., cooled, and diluted with water (25 c.c.) The *product* was collected, washed with water, dried, and crystallised from light petroleum (b. p. 60—80°), giving orange-yellow prisms (1·45 g.), m. p. 101·5—102·5° (Found : C, 77·8; H, 6·7; N, 15·9. $C_{17}H_{17}N_3$ requires C, 77·56; H, 6·45; N, 15·97%).

2-*Piperidino*-5 : 6-*benzoquinoxaline*, prepared similarly from 2-chloro-5 : 6-benzoquinoxaline, was purified by chromatography (benzene–light petroleum; alumina) and formed lemon-yellow rhombic prisms, m. p. 124—125° (Found : C, 77·9; H, 6·5; N, 15·7%).

*Dichloro*-5 : 6-*benzoquinoxaline*. Chlorine was passed slowly into 5 : 6-benzoquinoxaline (2·3 g.), dissolved in glacial acetic acid (10 c.c.), during 1 hr., and the solution was filtered from 5 : 6-benzoquinoxaline hydrochloride (0·2 g.) and diluted with water. The pasty precipitate was triturated with aqueous sodium carbonate and with water, and crystallised from benzene and then (twice) from *cyclo*hexane, to give a colourless *product*, m. p. 187—188° (Found : C, 57·9; H, 1·7; N, 11·0. $C_{12}H_6N_2Cl_2$ requires C, 57·8; H, 2·4; N, 11·25%).

3-*Hydroxy*-1-*methyl*-6- *or* -7-*nitroquinoxal*-2-*one*. 2 : 3-Dihydroxy-6-nitroquinoxaline (2·0 g.), 5% sodium hydroxide solution (115 c.c.), and methyl sulphate (5 c.c.) were stirred for 16 hr., and the sodium salt was collected after 48 hr., dissolved in boiling water (100 c.c.) (carbon), and precipitated with acetic acid. The *product* crystallised from dilute acetic acid as yellow crystals, m. p. 344° (Found : C, 48·7; H, 3·1; N, 18·8. $C_9H_9O_4N_3$ requires C, 48·87; H, 3·16; N, 19·0%).

Similarly, methylation of 6-cyano-2 : 3-dihydroxyquinoxaline (m. p. >360°) gave 6- or 7-*cyano*-3-*hydroxy*-1-*methylquinoxal*-2-*one*, colourless needles (from dilute acetic acid), m. p. 353—354° (Found : C, 59·3; H, 3·4; N, 20·6. $C_{10}H_7O_2N_3$ requires C, 59·7; H, 3·5; N, 20·9%).

Some of the work described in this paper is incorporated in B.P.666,197 and B.P.684,346.

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## 568. *Quinoxaline N-Oxides. Part II.* Oxides of Py-Substituted Quinoxalines.*

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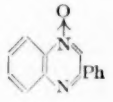
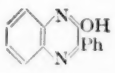
*N*-Oxides of quinoxalines bearing alkyl, aralkyl, or aryl groups in the 2- and 3-positions are prepared. Steric hindrance to *N*-oxidation is caused by *iso*propyl or aryl groups, and by substituents in the 5-position. Hydrogenation of 2-styrylquinoxalines over Raney nickel gives 2-aralkylquinoxalines, or 2-aralkyl-1 : 2 : 3 : 4-tetrahydroquinoxalines if the 3-position is unoccupied. The reaction of ethylmagnesium bromide with 2 : 3-dihydroxyquinoxaline and with 1 : 2 : 3 : 4-tetrahydro-1 : 4-dimethyl-2 : 3-dioxoquinoxaline is described.

In Part I* the oxidation of quinoxaline derivatives with organic peracids, particularly with 1·2M-peracetic acid in acetic acid, is described. Under similar conditions 2-ethyl- and 2 : 3-di(lower alkyl)-quinoxalines are readily oxidised to the corresponding 1 : 4-dioxides, but 2-methyl-3-*iso*propylquinoxaline gives a considerable proportion of mono-*N*-oxide, and 2 : 3-di*iso*propylquinoxaline is unchanged by hot peracetic or performic acid. Examination of models shows that the *iso*propyl group is likely to cause steric hindrance.

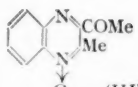
Maffei (*Gazzetta*, **1946**, **76**, 239; see also Linsker and Evans, *J. Amer. Chem. Soc.*, **1946**, **68**, 403) claimed that oxidation of 2 : 3-diphenylquinoxaline with hydrogen peroxide in acetic acid gives 2 : 3-diphenylquinoxaline 1 : 4-dioxide, but the main product under the conditions he described proved to be 2 : 3-diphenylquinoxaline 1-oxide. With more concentrated peracetic acid, mixtures yielding 50—60% of monoxide and 25—45% of dioxide are obtained. 2 : 3-Di-*p*-methoxyphenylquinoxaline on oxidation gives 65% of mono-*N*-oxide and 10—15% of di-*N*-oxide. 2-Phenylquinoxaline with peracetic or performic acid gives a monoxide, which we regard as 2-phenylquinoxaline 4-oxide (I), and



(I)



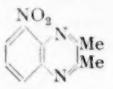
(II)



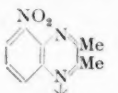
(III)

only traces of 2-phenylquinoxaline 1 : 4-dioxide; (I) is not oxidised further to the dioxide, but on prolonged treatment with peracetic acid gives 2-hydroxy-3-phenylquinoxaline (II) and other (unidentified) substances. This is surprising since 2-phenyl-3-methylquinoxaline readily yields a di-*N*-oxide. Other groups in the 2-position which prevent the attachment of oxygen to the adjacent nitrogen atom are Cl (Part I), OH, OEt, and $CO_2H$ (Newbold and Spring, *J.*, **1948**, 519). 2-Acetyl-3-methylquinoxaline affords only a mono-*N*-oxide (III).

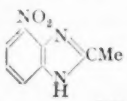
Oxidation of 2 : 3-dimethylquinoxalines substituted in the carbocyclic nucleus resembles that of the related 2 : 3-unsubstituted compounds, the steric hindrance from groups in the 5-position being more pronounced. 2 : 3-Dihydroxy-compounds are not formed as by-



(IV)



(V)



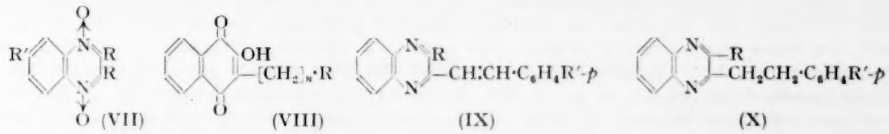
(VI)

products, and moderate yields of 2 : 3-dimethyl-6-nitro- and 6-cyano-2 : 3-dimethylquinoxaline 1 : 4-dioxide are obtainable. Peracetic acid oxidation of 2 : 3-dimethyl-5-nitroquinoxaline (IV) gives the monoxide (V) and 2-methyl-4-nitrobenziminazole (VI). Only the mono-*N*-oxide has been obtained from 6 : 7-dichloro-2 : 3-dimethylquinoxaline.

The methyl groups in 2 : 3-dimethylquinoxaline 1 : 4-dioxide do not show the enhanced reactivity of quinaldine methiodide, there being no reaction with reagents such as *p*-di-

* Part I, preceding paper.

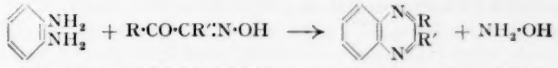
methylaminobenzaldehyde. Methyl iodide reacts slowly with 2 : 3-dimethylquinoxaline 1-oxide in boiling acetonitrile, giving a dark quaternary salt, but no methiodide was obtained from 2 : 3-diphenylquinoxaline 1-oxide. Vivian (*J. Amer. Chem. Soc.*, 1949, **71**, 1139) showed that the chlorine atom in 2-chlorophenazine di-*N*-oxide is labile, but attempts to demonstrate similar reactivity in 6-chloro-2 : 3-dimethylquinoxaline 1 : 4-dioxide by condensation with piperidine or 3-piperidinopropylamine gave no definite result. 6-Aminoquinoxaline 1 : 4-dioxide and 6-amino-2 : 3-dimethylquinoxaline 1 : 4-dioxide which are obtained by acid hydrolysis of the 6-acetamido-compounds gave no characterisable derivatives with a number of usual reagents for aromatic amines, and, although they could be diazotised, the replacement of the diazonium group by halogen was unsatisfactory. A few derivatives (VII; R = Me, R′ = *p*-Me·$C_6H_4$·$SO_2$·NH, *p*-NHAc·$C_6H_4$·$SO_2$·NH, and 2-amino-1 : 6-dimethylpyrimidinium-4-amino) have been obtained.



(VII) (VIII) (IX) (X)

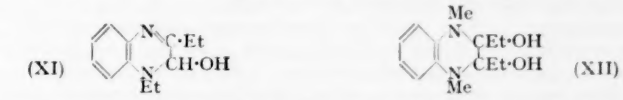
In view of the antimalarial activity of certain 2-hydroxy-1 : 4-naphthaquinones (VIII) bearing large alkyl or aralkyl groups in the 3-position (Fieser *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3151 *et seq.*), the preparation of some analogously constituted quinoxaline 1 : 4-dioxides was attempted. Hydrogenation of the mono- and di-styryl derivatives obtained from 2 : 3-dimethylquinoxaline and *p*-chlorobenzaldehyde (IX; R = Me or CH:CH·$C_6H_4$Cl, R′ = Cl) over Raney nickel gave the corresponding 2-*p*-chlorophenylethyl derivatives (X; R = Me or $CH_2$·$CH_2$·$C_6H_4$Cl, R′ = Cl) from which di-*N*-oxides were made. Similarly, (IX; R = Me, R′ = OMe) and (IX; R = OH, R′ = Cl) were reduced to (X; R = Me, R′ = OMe) and (X; R = OH, R′ = Cl), but hydrogenation of 2-styrylquinoxalines unsubstituted in the 3-position gave 1 : 2 : 3 : 4-tetrahydro-2-2′-phenylethylquinoxalines. 2-2′-Ethoxyethyl-3-methylquinoxaline and 2-methyl-3-2′-phenoxyethylquinoxaline gave di-*N*-oxides, but attempts to convert these into the corresponding 2-bromoethyl derivatives were unsuccessful.

Condensation of hydroxyimino-ketones with *o*-phenylenediamine proceeds according to the following scheme (Henderson, *J.*, 1929, 466), the product in some cases being a molecular compound of the quinoxaline with the dioxime (separable into its components by treatment with alkali). In spite of the loss occasioned by this side reaction no improve-



$NH_2$·OH + R·CO·CR′:N·OH ⟶ HO·N:CR·CR′:N·OH

ment in overall yield was obtained by first hydrolysing the hydroxyimino-ketone to the 1 : 2-diketone and condensing the latter with *o*-phenylenediamine. Oxidation of acyloins with cupric acetate in acetic acid (Bloch, Lehr, Erlenmeyer, and Vogler, *Helv. Chim. Acta*, 1945, **28**, 1410) is a most satisfactory preparative method for symmetrical 1 : 2-diketones.



(XI) (XII)

Some alternative methods of preparing 2 : 3-dialkylquinoxalines were examined. Reaction of ethylmagnesium bromide with 2 : 3-dihydroxyquinoxaline gave a little 2 : 3-diethylquinoxaline, together with 2-ethyl-3-hydroxyquinoxaline and a compound, m. p. 158—160°, tentatively regarded as 1 : 3-diethyl-1 : 2-dihydro-2-hydroxyquinoxaline (XI). Molecular-weight determinations on this compound gave anomalous results, and attempts to acetylate it or to oxidise it to 1 : 3-diethylquinoxal-2-one were unsuccessful. It was also obtained in small yield from ethylmagnesium bromide and 2 : 3-dichloroquinoxaline, no 2 : 3-diethylquinoxaline being isolated in this case [Ogg and Bergstrom (*J. Amer. Chem.*

*Soc.*, 1931, **53**, 1846) prepared 2 : 3-di-*n*-propylquinoxaline from propylmagnesium bromide and 2 : 3-dichloroquinoxaline]. 1 : 2 : 3 : 4-Tetrahydro-1 : 4-dimethyl-2 : 3-dioxoquinoxaline and ethylmagnesium bromide gave a rather intractable product which analysed as a hydrate of 2 : 3-diethyl-1 : 2 : 3 : 4-tetrahydro-2 : 3-dihydroxy-1 : 4-dimethylquinoxaline (XII) and gave hexane-3 : 4-dione on acid hydrolysis.

## Experimental

*3-Hydroxyimino-1-phenoxypentan-4-one.*—Ethyl α-2-phenoxyethylacetoacetate (Robinson and Watt, *J.*, 1934, 1536) (83 g.), water (385 c.c.), and potassium hydroxide (21 g.) were stirred overnight in a closed flask, and the aqueous layer was separated from undissolved ester (17 g.), washed with ether, and added to sodium nitrite (23 g.) in water (80 c.c.). The solution was cooled, stirred, and treated dropwise with 20% sulphuric acid at $<10°$ until acid to Congo-red. After 5 min. the mixture was made alkaline with sodium hydroxide solution and extracted with ether (500 c.c.), and the ether was washed repeatedly with dilute sodium hydroxide solution until the latter was no longer yellow. The combined alkaline solutions were acidified and extracted with ether. Evaporation of the dried ($Na_2SO_4$) extract gave *3-hydroxyimino-1-phenoxypentan-4-one* (46 g.), m. p. *ca.* 60°, which formed colourless needles, m. p. 66—67°, from light petroleum (Found : N, 6·85. $C_{11}H_{13}O_3N$ requires N, 6·75%). When distilled with 20% sulphuric acid it gave a solid (pale yellow plates, m. p. 51—52°, from light petroleum) which was not the required diketone.

The following hydroxyimino-ketones were made by the same method : hydroxyiminoacetone, 1-hydroxyiminobutan-2-one, m. p. 53—54° (Sharp and Spring, *J.*, 1948, 1862, found m. p. 55°), 3-hydroxyiminopentan-2-one, 3-hydroxyiminoheptan-4-one, 1-ethoxy-3-hydroxyiminopentan-4-one (Tota and Elderfield, *J. Org. Chem.*, 1942, **7**, 313), and 3-hydroxyiminooctan-2-one. 1-Hydroxyimino-1-phenylpropan-2-one was obtained from hydroxyiminoacetone and benzenediazonium chloride (Borsche, *Ber.*, 1907, **40**, 737).

*Quinoxalines.*—The following exemplify the general methods of preparation used.

(*a*) *o*-Phenylenediamine (67·5 g.), dissolved in hot water (750 c.c.), was treated with diacetyl (55 c.c.) and heated on the steam-bath 1 hr. 2 : 3-Dimethylquinoxaline dihydrate was filtered off when cold, and dried by azeotropic distillation with benzene, and the anhydrous compound was crystallised from light petroleum (b. p. 100—120°) (yield, 73·5 g. ; m. p. 104°).

(*b*) 4-Chloro-*o*-phenylenediamine (71 g.) was heated in 10% (v/v) aqueous acetic acid (600 c.c.) on the steam-bath with diacetyl (44 c.c.) for 1 hr., then was made alkaline to Clayton Yellow paper with aqueous sodium hydroxide, and *6-chloro-2 : 3-dimethylquinoxaline* was isolated by steam-distillation.

In some instances the diamine hydrochloride and sodium acetate were used; less volatile quinoxalines were isolated by filtration and then distilled or recrystallised.

(*c*) 3-Hydroxyiminopentan-2-one (41 g.) was added to *o*-phenylenediamine (40 g.) dissolved in acetic acid (32·4 c.c.), water (112 c.c.), and concentrated hydrochloric acid (16·7 c.c.), and the mixture was boiled for 3 min., cooled, and filtered. 2-Ethyl-3-methylquinoxaline was extracted from this solid and from the aqueous filtrate with light petroleum (b. p. 60—80°), and the extract was washed with 2% sulphuric acid, 5% sodium hydroxide solution, and water, dried ($Na_2SO_4$), and distilled (yield, 20 g.). The residual solid (31·7 g.) was 2 : 3-dihydroxyiminopentane, colourless needles (from benzene), m. p. 171° (Found : C, 46·3; H, 7·7; N, 21·0. Calc. for $C_5H_{10}O_2N_2$ : C, 46·2; H, 7·7; N, 21·5%). In other preparations the hydrochloric acid was omitted and the reaction time was increased to 1—1·5 hr.

(*d*) *o*-Phenylenediamine (130 g.), 1-ethoxy-3-hydroxyiminopentan-4-one (151 g.) and 40% sodium hydrogen sulphite solution (525 c.c.) were stirred at 60° for 3 hr., and the solid product was collected when cold, washed with water, extracted with cold 5% sodium hydroxide solution, and crystallised from acetone or benzene, giving 2-2′-ethoxyethyl-3-methylquinoxaline (72 g.). Acidification of the alkaline extract gave *5-ethoxy-2 : 3-dihydroxyiminopentane* (30 g.), colourless platelets (from benzene), m. p. 126° (Found : C, 48·5; H, 7·85; N, 15·4. $C_7H_{14}O_3N_2$ requires C, 48·3; H, 8·05; N, 16·1%).

The following dioximes were isolated from reactions of types (*c*) and (*d*) :

Methylglyoxime, isolated as its *molecular compound* with 2 : 6 : 7-trimethylquinoxaline, m. p. 148° (from aqueous ethanol) (Found : C, 60·8; H, 6·5; N, 20·6. $C_{11}H_{12}N_2,C_3H_6O_2N_2$ requires C, 61·3; H, 6·55; N, 20·4%).

Ethylglyoxime, microscopic white needles (from light petroleum), m. p. 126—128° (Found : N, 24·0. Calc. for $C_4H_8O_2N_2$ : N, 24·15%).

2 : 3-Dihydroxyimino-octane, white plates (from benzene), m. p. 170° (Found : C, 55·9; H, 9·3; N, 15·9. Calc. for $C_8H_{16}O_2N_2$ : C, 55·8; H, 9·3; N, 16·3%) (isolated, but not identified by McIlwain, *J.*, 1943, 322).

Phenylglyoxal dioxime, obtained as its *molecular compound* with 2-phenylquinoxaline, fine white needles (from ethanol), m. p. 131° (Found : C, 71·6; H, 4·9; N, 14·9. $C_{14}H_{10}N_2,C_8H_8O_2N_2$ requires C, 71·35; H, 4·85; N, 15·1%). This substance was formed from hydroxyiminoacetophenone and *o*-phenylenediamine in ethanol, but not in aqueous acetic acid.

In addition to the new quinoxalines listed in Table 1 the following were prepared by the method indicated : 2 : 3-dimethylquinoxaline (*a*) (Gabriel and Sonn, *Ber.*, 1907, **40**, 4852), 2-ethyl-3-methylquinoxaline (*a*, *c*) (Heilbron, Jones, Smith, and Weedon, *J.*, 1946, 54), 2-methyl-3-*n*-propylquinoxaline (*a*) (*idem*, *loc. cit.*), 2-methyl-3-*iso*propylquinoxaline (*a*), m. p. 40—42° (Pauly and Lieck, *Ber.*, 1900, **33**, 500, found m. p. 37°), 2-methyl-3-phenylquinoxaline (*c*) (von Auwers, *Ber.*, 1917, **50**, 1177), 2-benzyl-3-methylquinoxaline (Moureu, *Ann. Chim.*, 1930, **14**, 352), 2 : 3-diethylquinoxaline (*a*) (Urion, *ibid.*, 1934, **1**, 55), 2 : 3-di-*n*-propylquinoxaline (*a*) (Ogg and Bergstrom, *loc. cit.*), 2-phenylquinoxaline (*a*, *c*) (Hinsberg, *Annalen*, 1896, **292**, 246),

TABLE 1. *Alkylquinoxaline derivatives.*

| Substituents | Method of prepn. | Formula | M. p. | Found, % C | Found, % H | Found, % N | Required, % C | Required, % H | Required, % N |
|---|---|---|---|---|---|---|---|---|---|
| 2-Ethyl | *c* | $C_{10}H_{10}N_2$ | (i) | 75·2 | 6·2 | 17·4 | 75·9 | 6·3 | 17·7 |
| 2-Ethyl-3-*n*-propyl | *a* | $C_{13}H_{16}N_2$ | 45° | — | — | 14·1 | — | — | 14·0 |
| 2 : 3-Di*iso*propyl | *a* | $C_{14}H_{18}N_2$ | 74 | 78·4 | 8·2 | — | 78·5 | 8·4 | — |
| 2-2′-Ethoxyethyl-3-methyl | *d* | $C_{13}H_{16}ON_2$ | 64 | 71·9 | 7·55 | 13·1 | 72·2 | 7·4 | 13·0 |
| 2-Methyl-3-2′-phenoxyethyl | *d* | $C_{17}H_{16}ON_2$ | 156—156·5 | 77·65 | 6·1 | 10·2 | 77·27 | 6·05 | 10·6 |
| 2 : 3 : 5-Trimethyl | *a* | $C_{11}H_{12}N_2$ | 72—73 (ii) | — | — | 16·5 | — | — | 16·3 |
| 2 : 6 : 7-Trimethyl | *c* | $C_{11}H_{12}N_2$ | 116 | 76·7 | 6·9 | 16·1 | 76·75 | 6·95 | 16·3 |
| 2 : 3 : 6 : 7-Tetramethyl | *b* | $C_{12}H_{14}N_2$ | 189—190 | — | — | 14·8 | — | — | 14·5 |
| 2 : 3-Dimethyl-5 : 6-benzo | *a* | $C_{14}H_{12}N_2$ | 101 | — | — | 13·6 | — | — | 13·5 |
| 5-Methoxy-2 : 3-dimethyl | *a* | $C_{11}H_{12}ON_2$ | 118 | — | — | 14·3 | — | — | 14·9 |
| 5-Ethoxy-2 : 3-dimethyl | *b* | $C_{12}H_{14}ON_2$ | 90—92 | — | — | 13·8 | — | — | 13·9 |
| 6-Ethoxy-2 : 3-dimethyl | *b* | $C_{12}H_{14}ON_2$ | 107—109 | — | — | 13·8 | — | — | 13·9 |
| 5 : 6-Dimethoxy-2 : 3-dimethyl | *a* | $C_{12}H_{14}O_2N_2$ | 105—107 | — | — | 13·3 | — | — | 12·85 |
| 6 : 7-Dimethoxy-2 : 3-dimethyl | *b* | $C_{12}H_{14}O_2N_2$ | 173—174 | — | — | 12·7 | — | — | 12·85 |
| 5-Chloro-2 : 3-dimethyl | *b* | $C_{10}H_9N_2Cl$ | 78—80 (iii) | — | — | 14·6 | — | — | 14·55 |
| 6-Chloro-2 : 3-dimethyl | *b* | $C_{10}H_9N_2Cl$ | 91—92 | — | — | 14·7 | — | — | 14·55 |
| 6-Bromo-2 : 3-dimethyl | *b* | $C_{10}H_9N_2Br$ | 84—85 | — | — | 12·3 | — | — | 11·8 |
| 6-Iodo-2 : 3-dimethyl | *b* | $C_{10}H_9N_2I$ | 75—75·5 | — | — | 10·3 | — | — | 9·85 |
| 6-Chloro-2 : 3 : 7-trimethyl | *b* | $C_{11}H_{11}N_2Cl$ | 154 | 64·4 | 5·5 | 14·2 | 63·9 | 5·3 | 13·6 |
| 6-Bromo-2 : 3 : 7-trimethyl | *b* | $C_{11}H_{11}N_2Br$ | 145 | — | — | 11·4 | — | — | 11·15 |
| 5 : 8-Dichloro-2 : 3-dimethyl | *b* | $C_{10}H_8N_2Cl_2$ | 146—148 | — | — | 12·2 | — | — | 12·3 |
| 6 : 7-Dichloro-2 : 3-dimethyl | *b* | $C_{10}H_8N_2Cl_2$ | 191—192 | 52·9 | 3·4 | 12·5 | 52·8 | 3·5 | 12·3 |
| 2 : 3-Dimethyl-5-nitro | *b* | $C_{10}H_9O_2N_3$ | 131—131·5 | — | — | 20·3 | — | — | 20·7 |
| 2 : 3-Dimethyl-6-nitro | *b* | $C_{10}H_9O_2N_3$ | 133—134 | — | — | 21·2 | — | — | 20·7 |
| 2 : 3-Dimethyl-6-trifluoromethyl | *b* | $C_{11}H_9N_2F_3$ | 93 | — | — | 12·5 | — | — | 12·4 |
| 6-Cyano-2 : 3-dimethyl | *a* | $C_{11}H_9N_3$ | 199—200 | — | — | 22·6 | — | — | 22·95 |

(i) B. p. 97—100°/3 mm. (ii) B. p. 134—137°/10 mm. (iii) B. p. 158°/10 mm.

2 : 3-diphenylquinoxaline (Hinsberg and König, *Ber.*, 1894, **27**, 2181), 2 : 3-di-*p*-methoxyphenylquinoxaline (Bost and Towell, *J. Amer. Chem. Soc.*, 1948, **70**, 903), 6-methoxy-2 : 3-dimethylquinoxaline (*a*) (*idem*, *loc. cit.*), 6-amino-2 : 3-dimethylquinoxaline (*b*) (Gilman and Broadbent, *ibid.*, p. 2619), 2 : 3 : 6-trimethylquinoxaline (*a*) (von Pechmann, *Ber.*, 1888, **21**, 1411), and 2-acetyl-3-methylquinoxaline (*a*) (Sachs and Barschall, *Ber.*, 1901, **34**, 3054).

6-*Acetamido*-2 : 3-*dimethylquinoxaline* (first prepared in these laboratories by Dr. A. F. Crowther). 6-Amino-2 : 3-dimethylquinoxaline (1·5 g.), acetic anhydride (11·5 c.c.), and benzene (150 c.c.) were boiled under reflux for 1 hr. On cooling, the *product* (1·6 g.) crystallised; it had m. p. 192—193° (Found : C, 67·1; H, 6·05; N, 19·7. $C_{12}H_{13}ON_3$ requires C, 67·0; H, 6·05; N, 19·5%).

6-p-*Acetamidobenzenesulphonamido*-2 : 3-*dimethylquinoxaline*. 6-Amino-2 : 3-dimethylquinoxaline (3·45 g.) was treated at room temperature with *p*-acetamidobenzenesulphonyl chloride (4·7 g.) in pyridine (20 c.c.). After 5 hr. the pyridine was distilled off under reduced pressure and the residue was washed well with dilute hydrochloric acid and extracted with 8% sodium hydroxide solution (100 c.c.). The extract was clarified by carbon and treated with 50% acetic acid to precipitate crude 6-p-*acetamidobenzenesulphonamido*-2 : 3-*dimethylquinoxaline* (3·65 g.; m. p. 310—312°) which was best purified by re-treatment with alkali and acid,

forming colourless, microscopic prisms, m. p. 315—316° (decomp.) (Found: C, 54·8; H, 5·05; N, 13·85. $C_{18}H_{18}O_3N_4S,1{\cdot}5H_2O$ requires C, 54·5; H, 5·3; N, 14·2%).

*Reaction of* 6-*aminoquinoxaline with diethylmalonyl chloride.* 6-Aminoquinoxaline (17·6 g.) in pyridine (120 c.c.), treated with diethylmalonyl chloride (12 g.) at room temperature, gave NN′-*di*-6-*quinoxalinyldiethylmalonamide* (1·5 g.), which formed cream prisms, m. p. 213—214°, from *n*-propanol (Found: C, 66·35; H, 5·1; N, 20·95. $C_{23}H_{22}O_2N_6$ requires C, 66·65; H, 5·35; N, 20·3%), and 6-*diethylmalonimidoquinoxaline* (7·8 g.), which crystallised as minute colourless prisms, m. p. 73—74°, from aqueous ethanol [Found: C, 66·95; H, 5·3; N, 15·6; 15·55%; *M* (Rast), 240, 245, 235. $C_{15}H_{15}O_2N_3$ requires C, 66·9; H, 5·6; N, 15·6%; *M*, 269]. The latter compound did not react with 6-aminoquinoxaline, but, heating it in an excess of aniline at 170° for 30 min. gave N-*phenyl*-N′-6-*quinoxalyldiethylmalonamide*, m. p. 206—207° (from methanol) (Found: C, 69·6; H, 6·05; N, 15·65. $C_{21}H_{22}O_2N_4$ requires C, 69·6; H, 6·1; N, 15·45%).

6-*Diethylmalonimido*-2 : 3-*dimethylquinoxaline*, prepared in a similar manner from 6-amino-2 : 3-dimethylquinoxaline, crystallised from aqueous ethanol as colourless needles, m. p. 96—97° (Found: C, 68·3; H, 6·35; N, 14·2. $C_{17}H_{19}O_2N_3$ requires C, 68·7; H, 6·45; N, 14·15%).

*Reaction of* 2 : 3-*dihydroxyquinoxaline with ethylmagnesium bromide.* Dry, powdered 2 : 3-dihydroxyquinoxaline (35 g.) was added to ethylmagnesium bromide prepared from magnesium (24 g.) and ethyl bromide (109 g.) in ether (500 c.c.), and the mixture was stirred and refluxed for 36 hr., and then treated with water (250 c.c.) and saturated ammonium chloride solution (250 c.c.). The ethereal layer was separated and the aqueous layer and undissolved solid were extracted with ether (800 c.c.). The insoluble material (4·8 g.) was collected, washed with dilute hydrochloric acid, and dried. It melted above 300°, but on methylation it gave 3-ethyl-1 : 2-dihydro-1-methyl-2-oxoquinoxaline (see below). The ethereal solutions were extracted twice with 2N-sodium hydroxide (250 c.c.) and then with water (250 c.c.), and the aqueous extracts were acidified, to precipitate 2-*ethyl*-3-*hydroxyquinoxaline* (1·9 g.; m. p. 190°) which crystallised from light petroleum (b. p. 80—100°) in colourless needles, m. p. 194—196° (Found: C, 69·05; H, 5·55; N, 15·8. $C_{10}H_{10}ON_2$ requires C, 68·95; H, 5·75; N, 16·1%). Evaporation of the dried ($Na_2SO_4$) ethereal layer gave a red syrup which crystallised slowly, and on recrystallisation from light petroleum (b. p. 80—100°) gave a *substance* (*ca.* 8 g.), m. p. 158—160° [Found: C, 70·4; H, 8·25; N, 13·45%; *M* (ebullioscopic), 266—283 (in benzene), 125 (in methanol), 137—153 (in ethanol). $C_{12}H_{16}ON_2$ requires C, 70·5; H, 7·8; N, 13·7%; *M*, 204]. Evaporation of the mother-liquor and chromatographic purification (benzene–light petroleum; alumina) gave 2 : 3-diethylquinoxaline (0·7 g.), m. p. and mixed m. p. 48—49° (Found: N, 15·5. Calc. for $C_{12}H_{14}N_2$: N, 15·05%), a red oil (6·0 g.), and 2-ethyl-3-hydroxyquinoxaline (1·0 g.).

3-*Ethyl*-1 : 2-*dihydro*-1-*methyl*-2-*oxoquinoxaline.* 2-Ethyl-3-hydroxyquinoxaline, dissolved in sodium hydroxide solution, was shaken with methyl sulphate at room temperature. The *product* separated in long yellow needles, m. p. 106°, from its colourless aqueous solution (Found: C, 70·3; H, 6·45; N, 15·2. $C_{11}H_{12}ON_2$ requires C, 70·2; H, 6·4; N, 14·9%).

*Reaction of* 1 : 2 : 3 : 4-*tetrahydro*-1 : 4-*dimethyl*-2 : 3-*dioxoquinoxaline with ethylmagnesium bromide.* 1 : 2 : 3 : 4-Tetrahydro-1 : 4-dimethyl-2 : 3-dioxoquinoxaline (39 g.), suspended in ether (250 c.c.), was added gradually to the Grignard reagent from magnesium (12·5 g.) and ethyl bromide (55 g.) in ether (200 c.c.). When the vigorous reaction had subsided the mixture was stirred and refluxed for 6 hr., cooled, and decomposed with ammonium chloride solution. Evaporation of the ethereal layer gave a syrup which partly crystallised after several weeks. The solid was collected, washed with benzene, and crystallised from ethyl acetate. 2 : 3-*Diethyl*-1 : 2 : 3 : 4-*tetrahydro*-2 : 3-*dihydroxy*-1 : 4-*dimethylquinoxaline trihydrate* formed colourless needles, m. p. 54—55° (Found: C, 55·25; H, 8·6; N, 9·5; loss over $P_2O_5$ in a vacuum-desiccator, 15·7. $C_{14}H_{22}O_2N_2,3H_2O$ requires C, 55·25; H, 9·2; N, 9·2; $H_2O$, 17·75%). When distilled with 10% (v/v) sulphuric acid it gave hexane-3 : 4-dione, characterised by conversion into 2 : 3-diethylquinoxaline.

*Condensation of* 2 : 3-*dimethylquinoxaline with* p-*chlorobenzaldehyde.* 2 : 3-Dimethylquinoxaline (7·9 g.), *p*-chlorobenzaldehyde (7·0 g.), and acetic anhydride (25 c.c.) were heated under reflux in an oil-bath at 160° for 3 hr. When cold, the solid (3·4 g.) was filtered off, dried, and crystallised from 2-ethoxyethanol and then from benzene, to give 2 : 3-di-*p*-chlorostyrylquinoxaline, m. p. 216° (Bennett and Willis, *J.*, 1928, 1960). The mother-liquors from the reaction were steam-distilled to remove unchanged *p*-chlorobenzaldehyde, and the non-volatile residue was extracted with ether. Evaporation of the dried ($K_2CO_3$) extract and crystallisation from methanol gave 3-p-*chlorostyryl*-2-*methylquinoxaline* (4·8 g.), yellow needles, m. p. 109—110° (Found: C, 72·3; H, 4·6; N, 9·7. $C_{17}H_{13}N_2Cl$ requires C, 72·7; H, 4·65; N, 10·0%).

The following compounds were made similarly :

2-*Styrylquinoxaline*, orange-yellow rods [from light petroleum (b. p. 80—100°)], m. p. 105° (Found : C, 82·3; H, 5·3; N, 12·0. $C_{16}H_{12}N_2$ requires C, 82·7; H, 5·2; N, 12·1%).

2-p-*Chlorostyrylquinoxaline*, pale yellow needles [from light petroleum (b. p. 80—100°)], m. p. 143° (Found : C, 71·7; H, 4·4; N, 10·3. $C_{16}H_{11}N_2Cl$ requires C, 72·0; H, 4·1; N, 10·5%).

3-p-*Chlorostyryl*-2-*hydroxyquinoxaline*, yellow needles (from acetic acid), m. p. 273—273·5° (Found : C, 68·1; H, 3·6; N, 10·5. $C_{16}H_{11}ON_2Cl$ requires C, 68·0; H, 3·9; N, 9·9%).

2-*p*-Methoxystyryl-3-methyl- and 2 : 3-di-*p*-methoxystyryl-quinoxaline were made similarly, following the method of McKee, McKee, and Bost (*J. Amer. Chem. Soc.*, 1947, **69**, 468).

2-(2-p-*Chlorophenylethyl*)-3-*methylquinoxaline*. 2-*p*-Chlorostytyl-3-methylquinoxaline (2 g.) in ethanol (120 c.c.) was hydrogenated over Raney nickel at room temperature and pressure. When 1 equivalent of hydrogen had been absorbed, evaporation of the filtered solution gave a sticky yellow solid from which 2-(2-p-*chlorophenylethyl*)-3-*methylquinoxaline* was obtained by repeated crystallisation from light petroleum (b. p. 40—60°) as almost colourless rods, m. p. 106—106·5° (Found : C, 72·0; H, 5·2; N, 9·5. $C_{17}H_{15}N_2Cl$ requires C, 72·2; H, 5·3; N, 9·9%).

The following compounds were prepared similarly :

2-(2-p-*Methoxyphenylethyl*)-3-*methylquinoxaline*, cream prisms (from methanol), m. p. 79·5° (Found : C, 77·2; H, 6·7; N, 9·6. $C_{18}H_{18}ON_2$ requires C, 77·7; H, 6·5, N, 10·1%).

2 : 3-*Di*-(2-p-*chlorophenylethyl*)*quinoxaline*, cream plates (from ethanol), m. p. 150—150·5° (Found : C, 70·5; H, 4·9; N, 6·8. $C_{24}H_{20}N_2Cl_2$ requires C, 70·75; H, 4·9; N, 6·9%).

1 : 2 : 3 : 4-*Tetrahydro*-2-2′-*phenylethylquinoxaline*, colourless rods [from light petroleum (b. p. 60—80°)], m. p. 68·5—69·5° (Found : C, 80·9; H, 7·4; N, 11·9. $C_{16}H_{18}N_2$ requires C, 80·6; H, 7·6; N, 11·8%).

2-(2-p-*Chlorophenylethyl*)-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, colourless plates [from light petroleum (b. p. 80—100°)], m. p. 103° (Found : C, 70·6, 70·1; H, 6·4, 5·8; N, 10·4. $C_{16}H_{17}N_2Cl$ requires C, 70·4; H, 6·3; N, 10·3%).

3-(2-p-*Chlorophenylethyl*)-2-*hydroxyquinoxaline*, pale buff needles (from methanol), m. p. 212—214° (Found : C, 67·5; H, 4·6; N, 10·1. $C_{16}H_{13}ON_2Cl$ requires C, 67·5; H, 4·6; N, 9·8%).

*Formation of N-Oxides.*—Quinoxaline 1 : 4-dioxides prepared by oxidation with 1·2M-peracetic acid at 50° (see Part I) are listed in Table 2. Quinoxaline mono-*N*-oxides and di-*N*-oxides not prepared by the standard method are described below.

TABLE 2. *Quinoxaline* 1 : 4-*dioxides prepared by means of peracetic acid.*

| Substituents | Formula | M. p. | Found, % | | | Required, % | | |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | C | H | N |
| 2-Ethyl | $C_{10}H_{10}O_2N_2$ | 150—152° | 63·4 | 4·8 | 14·6 | 63·15 | 5·25 | 14·7 |
| 2 : 3-Dimethyl | $C_{10}H_{10}O_2N_2$ | 189—190 | 63·5 | 5·3 | 14·7 | 63·15 | 5·25 | 14·7 |
| 2-Ethyl-3-methyl | $C_{11}H_{12}O_2N_2$ | 139—141 | 65·4 | 5·7 | 13·9 | 64·7 | 5·9 | 13·1 |
| 2-Methyl-3-*n*-propyl | $C_{12}H_{14}O_2N_2$ | 108—110 | 66·3 | 6·1 | 12·7 | 66·05 | 6·4 | 12·85 |
| 2-Methyl-3-*iso*propyl | $C_{12}H_{14}O_2N_2$ | 193—194 | 66·5 | 6·8 | 12·85 | 66·05 | 6·4 | 12·85 |
| 2-Methyl-3-phenyl | $C_{15}H_{12}O_2N_2$ | 193—194 | 71·5 | 4·7 | 11·2 | 71·4 | 4·75 | 11·1 |
| 2-Benzyl-3-methyl | $C_{16}H_{14}O_2N_2$ | 155 | 71·7 | 4·8 | 10·0 | 72·2 | 5·25 | 10·5 |
| 2-Methyl-3-(2-*p*-chlorophenylethyl) | $C_{17}H_{15}O_2N_2Cl$ | 168—169 | 65·0 | 5·1 | 8·8 | 64·85 | 4·8 | 8·9 |
| 2-2′-Ethoxyethyl-3-methyl | $C_{13}H_{16}O_3N_2$ | 117 | 62·55 | 6·6 | 11·25 | 62·9 | 6·45 | 11·3 |
| 2-Methyl-3-2′-phenoxyethyl | $C_{17}H_{16}O_3N_2$ | 146 | 68·75 | 5·5 | 9·6 | 68·9 | 5·4 | 9·45 |
| 2 : 3-Diethyl | $C_{12}H_{14}O_2N_2$ | 108—110 | 66·4 | 6·4 | 12·9 | 66·05 | 6·4 | 12·85 |
| 2-Ethyl-3-*n*-propyl | $C_{13}H_{16}O_2N_2,H_2O$ | 85—87 | 62·15 | 7·05 | 11·7 | 62·4 | 7·2 | 11·2 |
| 2 : 3-Di-*n*-propyl | $C_{14}H_{18}O_2N_2$ | 74—76 | 68·4 | 7·1 | 11·6 | 68·3 | 7·3 | 11·4 |
| 2 : 3-Di-(2-*p*-chlorophenylethyl) | $C_{24}H_{20}O_2N_2Cl_2$ | 150—151 | 65·5 | 4·8 | — | 65·5 | 4·55 | — |
| 2 : 3 : 6-Trimethyl | $C_{11}H_{12}O_2N_2$ | 154—155 | — | — | 13·6 | — | — | 13·7 |
| 2 : 6 : 7-Trimethyl | $C_{11}H_{12}O_2N_2$ | 185—187 | 64·65 | 5·9 | 13·7 | 64·6 | 5·9 | 13·7 |
| 5-Methoxy-2 : 3-dimethyl | $C_{11}H_{12}O_3N_2$ | 206—208 | 59·7 | 5·6 | 12·9 | 60·0 | 5·45 | 12·7 |
| 6-Methoxy-2 : 3-dimethyl | $C_{11}H_{12}O_3N_2$ | 197—198 | 59·5 | 5·4 | 13·1 | 60·0 | 5·45 | 12·7 |
| 6-Ethoxy-2 : 3-dimethyl | $C_{12}H_{14}O_3N_2$ | 160—162 | 61·75 | 6·1 | 12·25 | 61·5 | 6·0 | 11·95 |
| 6-Chloro-2 : 3-dimethyl | $C_{10}H_9O_2N_2Cl$ | 175—176 | 53·2 | 4·0 | 12·5 | 53·45 | 4·0 | 12·5 |
| 6-Bromo-2 : 3-dimethyl | $C_{10}H_9O_2N_2Br$ | 186—188 | 45·0 | 3·3 | 10·3 | 44·6 | 3·3 | 10·4 |
| 2 : 3-Dimethyl-6-trifluoromethyl | $C_{11}H_9O_2N_2F_3$ | 155—156 | 51·5 | 3·45 | 10·7 | 51·15 | 3·5 | 10·9 |
| 2 : 3-Dimethyl-6-nitro | $C_{10}H_9O_4N_3$ | 192—194 | 51·3 | 3·9 | 17·8 | 51·0 | 3·8 | 17·9 |
| 6-Cyano-2 : 3-dimethyl | $C_{11}H_9O_2N_3$ | 216—218 | 61·1 | 4·4 | 19·5 | 61·3 | 4·2 | 19·5 |
| 6-Acetamido-2 : 3-dimethyl | $C_{12}H_{13}O_3N_3$ | 259—260 | 58·3 | 5·25 | 16·7 | 58·3 | 5·25 | 17·0 |
| 6-Diethylmalonimido-2 : 3-dimethyl | $C_{17}H_{19}O_4N_3$ | 198—201 | 61·95 | 5·9 | 13·05 | 62·0 | 5·8 | 12·75 |
| 2 : 3 : 6 : 7-Tetramethyl | $C_{12}H_{14}O_2N_2$ | 247—249 | 65·8 | 6·3 | 12·7 | 66·05 | 6·4 | 12·85 |
| 6 : 7-Dimethoxy-2 : 3-dimethyl | $C_{12}H_{14}O_4N_2$ | 275—277 | 57·8 | 6·0 | 11·1 | 57·6 | 5·6 | 11·2 |
| 6-Chloro-2 : 3 : 7-trimethyl | $C_{11}H_{11}O_2N_2Cl$ | 250—252 | 54·85 | 4·65 | 11·75 | 55·35 | 4·6 | 11·7 |
| 6-Bromo-2 : 3 : 7-trimethyl | $C_{11}H_{11}O_2N_2Br$, $0·5C_2H_5·OH$ | 242—244 | 47·45 | 4·1 | 9·0 | 47·05 | 4·6 | 9·15 |

2 : 3-*Dimethylquinoxaline* 1-*oxide*. 2 : 3-Dimethylquinoxaline (7·9 g.) and 1·2M-peracetic acid (42 c.c., 1 equiv.) were heated at 50° overnight, poured on ice (150 g.), and neutralised with aqueous sodium hydroxide. The precipitated *monoxide* (5·2 g.; m. p. 55°) was collected, washed with water, and crystallised repeatedly from light petroleum (b. p. 100—120°), to give colourless needles, m. p. 92—93° (depressed to 82° by 2 : 3-dimethylquinoxaline) (Found : N, 16·6. $C_{10}H_{10}ON_2$ requires N, 16·1%). By extraction of the aqueous mother-liquors with chloroform a mixture of the mono- and di-*N*-oxides (3·2 g.) was recovered.

2 : 3 : 5-*Trimethylquinoxaline* 1-*oxide*. 2 : 3 : 5-Trimethylquinoxaline (5 g.) and 1·2M-peracetic acid (100 c.c.) were heated at 50° overnight, evaporated at 10—15 mm. to 15—20 c.c., poured on ice (50 g.), and neutralised with aqueous sodium hydroxide. The *product* (4 g.) was collected, washed with water, and crystallised from light petroleum (b. p. 80—100°) or *cyclo*hexane in colourless needles, m. p. 98—99° (Found : N, 14·7. $C_{11}H_{12}ON_2$ requires N, 14·9%).

The following were prepared similarly :

2 : 3-*Dimethyl*-5 : 6-*benzoquinoxaline* 1-*oxide*, colourless needles [from light petroleum (b. p. 100—120°)], m. p. 165—167° (Found : N, 12·8. $C_{14}H_{12}ON_2$ requires N, 12·5%).

5-*Chloro*-2 : 3-*dimethylquinoxaline* 1-*oxide*, colourless needles (from *cyclo*hexane), m. p. 114—116° (Found : C, 57·6; H, 4·5; N, 13·3. $C_{10}H_9ON_2Cl$ requires C, 57·55; H, 4·3; N, 13·4%).

6 : 7-*Dichloro*-2 : 3-*dimethylquinoxaline* 1-*oxide*, yellow laminæ (from ethanol), m. p. 238° (Found : C, 48·7, 49·0; H, 3·2, 3·3; N, 11·2; Cl, 28·6. $C_{10}H_8ON_2Cl_2$ requires C, 49·3; H, 3·3; N, 11·5; Cl, 29·2%).

2-*Acetyl*-3-*methylquinoxaline* 4-*oxide*, pale yellow needles (from *cyclo*hexane), m. p. 92—94° (Found : C, 65·3; H, 4·7; N, 14·2. $C_{11}H_{10}O_2N_2$ requires C, 65·3; H, 4·95; N, 13·9%).

5-*Methoxy*-2 : 3-*dimethylquinoxaline* 1-*oxide*. 5-Methoxy-2 : 3-dimethylquinoxaline (6 g.) and 1·2M-peracetic acid (120 c.c.) were heated at 50° overnight, evaporated at 10—15 mm., and neutralised with ice (200 g.) and sodium hydroxide solution. The product was extracted with chloroform and the dried ($Na_2SO_4$) extract evaporated. The waxy residue (6·9 g.) was extracted with boiling *cyclo*hexane (200 and 100 c.c.), leaving an insoluble residue of di-*N*-oxide (2 g.) (Table 3). The *mono*-N-*oxide* crystallised from *cyclo*hexane in cream needles, m. p. 155—156° (Found : N, 13·9. $C_{11}H_{12}O_2N_2$ requires N, 13·7%).

The following were obtained similarly as by-products in the preparation of the di-*N*-oxides :

2-*Methyl*-3-iso*propylquinoxaline* 1(?)-*oxide*, colourless rhombs (from *cyclo*hexane), m. p. 72—73° (Found : C, 71·45; H, 6·75; N, 13·8. $C_{12}H_{14}ON_2$ requires C, 71·25; H, 7·0; N, 13·85%).

2 : 6 : 7-*Trimethylquinoxaline mono*-N-*oxide*, yellow microcrystalline solid [from light petroleum (b. p. 100—120°)], m. p. 133—135° (Found : N, 15·05. $C_{11}H_{12}ON_2$ requires N, 14·9%).

6-*Cyano*-2 : 3-*dimethylquinoxaline mono*-N-*oxide*, yellow nodules (from *cyclo*hexane), m. p. 169—171° (Found : N, 21·0. $C_{11}H_9ON_3$ requires N, 21·1%).

2 : 3-*Dimethyl*-5-*nitroquinoxaline* 1-*oxide*. 2 : 3-Dimethyl-5-nitroquinoxaline (3·5 g.) in dry dioxan (35 c.c.) was added to a 0·5M-solution of monoperphthalic acid in ether (60 c.c.). After 60 hr. at room temperature the solution was evaporated under reduced pressure and the residue neutralised with aqueous sodium carbonate and extracted with chloroform. Evaporation of the extract and chromatographic purification (benzene–ethyl acetate ; alumina) gave unchanged 2 : 3-dimethyl-5-nitroquinoxaline (0·55 g.) and 2 : 3-*dimethyl*-5-*nitroquinoxaline* 1-*oxide* (1·05 g.), yellow prisms (from ethanol or benzene), m. p. 157—158° (Found : C, 54·7; H, 4·3; N, 19·4. $C_{10}H_9O_3N_3$ requires C, 54·8; H, 4·1; N, 19·2%). Oxidation of 2 : 3-dimethyl-5-nitroquinoxaline with peracetic acid gave the same *N*-oxide, together with 2-methyl-4-nitrobenziminazole, m. p. 215—216° (Found : C, 54·6; H, 4·1; N, 23·3. Calc. for $C_8H_7O_2N_3$ : C, 54·25; H, 3·95; N, 23·7%).

2 : 3-*Diphenylquinoxaline* 1-*oxide and* 1 : 4-*dioxide*. (*a*) 2 : 3-Diphenylquinoxaline (2·82 g.), glacial acetic acid (40 c.c.), and 30% hydrogen proxide (10 c.c.) were heated at 50° overnight, cooled, and filtered from almost pure 2 : 3-*diphenylquinoxaline* 1-*oxide* (0·65 g.; m. p. 196°). Dilution of the filtrate with water (50 c.c.) precipitated some impure monoxide (1·1 g.; m. p. 188°) and neutralisation of the mother-liquors with 40% sodium hydroxide solution and ice precipitated 2 : 3-diphenylquinoxaline 1 : 4-dioxide (0·9 g.) which crystallised from ethanol in large yellow prisms, m. p. 216° (Found : C, 76·4; H, 4·4. Calc. for $C_{20}H_{14}O_2N_2$ : C, 76·3; H, 4·45%). 2 : 3-Diphenylquinoxaline 1-oxide crystallised from ethanol or acetic acid in long pale yellow prisms, m. p. 197°, becoming red-orange on exposure to light (Found : C, 80·4; H, 4·7. $C_{20}H_{14}ON_2$ requires C, 80·5; H, 4·7%).

(*b*) 2 : 3-Diphenylquinoxaline (32 g.) and 1·2M-peracetic acid (400 c.c.) were heated at 50°

overnight, cooled, and diluted with water (400 c.c.) to precipitate the mono-*N*-oxide (20·4 g.; m. p. 192—193°). Further dilution with water (800 c.c.) precipitated di-*N*-oxide (9·9 g.; m. p. 209—211°), and neutralisation with 40% aqueous sodium hydroxide gave a further 6 g.

The following were prepared similarly :

2 : 3-*Di*-p-*methoxyphenylquinoxaline* 1-*oxide*, pale yellow needles (from ethanol), m. p. 156° (Found : N, 7·9. $C_{22}H_{18}O_3N_2$ requires N, 7·8%).

2 : 3-*Di*-p-*methoxyphenylquinoxaline* 1 : 4-*dioxide*, yellow prisms (from ethanol), m. p. 183—184° (Found : N, 7·5. $C_{22}H_{18}O_4N_2$ requires N, 7·5%).

2-*Phenylquinoxaline* 4-*oxide and* 1 : 4-*dioxide*. 2-Phenylquinoxaline (13 g.), anhydrous formic acid (150 c.c.), and 30% hydrogen peroxide (50 c.c.) were heated overnight at 50° (after checking the initial exothermic reaction by cooling), evaporated at 10—15 mm. to 50—60 c.c., and poured into ice water (200 c.c.). The monoxide, which separated as an oil, crystallised rapidly and was collected (13 g.; m. p. 135—137°) and washed with water. Neutralisation of the mother-liquor with aqueous sodium hydroxide precipitated the dioxide (0·8 g.), a small amount more being recovered from the aqueous solution by extraction with chloroform. 2-*Phenylquinoxaline* 4-*oxide* crystallised from ethanol in orange-yellow needles, m. p. 137—138° (Found : N, 13·2. $C_{14}H_{10}ON_2$ requires N, 12·6%). 2-*Phenylquinoxaline* 1 : 4-*dioxide* formed lemon-yellow needles (from ethanol), m. p. 202—203° (Found : C, 69·4; H, 4·7; N, 11·4. $C_{14}H_{10}O_2N_2$ requires C, 70·5; H, 4·2; N, 11·8%). Oxidation of 2-phenylquinoxaline 4-oxide with 1·2M-peracetic acid (60°, 96 hr.) gave a mixture containing 2-hydroxy-3-phenylquinoxaline, m. p. 242—243° (Found : C, 75·7; H, 5·2; N, 12·6. Calc. for $C_{14}H_{10}ON_2$ : C, 75·7; H, 4·5; N, 12·6%), and with 8M-peracetic acid (45—50°; 5 hr.) some 2-phenylbenziminazole, m. p. 281—283°, was obtained, but in no case did the further oxidation give di-*N*-oxide.

6-*Aminoquinoxaline* 1 : 4-*dioxide*. 6-Acetamidoquinoxaline 1 : 4-dioxide (Part I) was boiled under reflux with 10% hydrochloric acid for 20 min. The solution was then made slightly alkaline with aqueous sodium hydroxide and the *product* was collected. It formed orange needles, m. p. 245° (decomp.), from water (Found : C, 54·8; H, 4·25; N, 23·95. $C_8H_7O_2N_3$ requires C, 54·25; H, 4·0; N, 23·7%). The *hydrochloride* crystallised from dilute hydrochloric acid as small brownish-red prisms, m. p. 208° (decomp.) (Found : C, 45·1; H, 4·0; N, 19·9. $C_8H_7O_2N_3$,HCl requires C, 45·0; H, 3·8; N, 19·65%).

6-*Amino*-2 : 3-*dimethylquinoxaline* 1 : 4-*dioxide*, obtained similarly by hydrolysis of the acetyl derivative, formed yellow-orange needles (from water), decomp. 268° (Found : C, 58·65; H, 5·65; N, 20·35. $C_{10}H_{11}O_2N_3$ requires C, 58·5; H, 5·4; N, 20·5%). The *hydrochloride*, brown prisms from dilute hydrochloric acid, decomposed at 240° (Found : C, 49·4; H, 5·0; N, 16·95. $C_{10}H_{11}O_2N_3$,HCl requires C, 49·7; H, 5·0; N, 17·4%).

2 : 3-*Dimethyl*-6-p-*toluenesulphonamidoquinoxaline* 1 : 4-*dioxide*, obtained from 6-amino-2 : 3-dimethylquinoxaline 1 : 4-dioxide and excess of toluene-*p*-sulphonyl chloride in pyridine at 0—10°, formed pale yellow prisms (from dimethylformamide), decomp. *ca.* 276° (Found : C, 56·95; H, 4·9; N, 11·5. $C_{17}H_{17}O_4N_3S$ requires C, 56·8; H, 4·8; N, 11·7%).

6-p-*Acetamidobenzenesulphonamido*-2 : 3-*dimethylquinoxaline* 1 : 4-*dioxide*. 6-Aminoquinoxaline 1 : 4-dioxide and *p*-acetamidobenzenesulphonyl chloride (10% excess) were added alternately in small quantities to pyridine, stirred at 10°. The mixture was heated on the steam-bath for 45 min., cooled, filtered, and evaporated. After trituration with dilute hydrochloric acid the residue was dissolved in dilute sodium hydroxide solution (charcoal) and acidified with acetic acid. The precipitated *product* formed small yellow rods, decomp. *ca.* 290°, from ethylene glycol (Found : C, 53·0; H, 4·8; N, 13·7. $C_{18}H_{18}O_5N_4S$ requires C, 53·7; H, 4·5; N, 13·95%). This compound, also obtained in small yield by peracetic acid oxidation of 6-*p*-acetamidobenzenesulphonamido-2 : 3-dimethylquinoxaline, was hydrolysed by hot 10% hydrochloric acid to 6-p-*aminobenzenesulphonamido*-2 : 3-*dimethylquinoxaline* 1 : 4-*dioxide*, yellow prisms, decomp. 265° (Found : C, 52·6; H, 3·85; N, 14·9; S, 8·9. $C_{16}H_{16}O_4N_4S$ requires C, 53·3; H, 4·5; N, 15·55; S, 8·9%).

2-*Amino*-1 : 6-*dimethyl*-4-(2′ : 3′-*dimethyl*-6′-*quinoxalinyl*)*aminopyrimidinium iodide* 1′ : 4′-*dioxide*. 6-Amino-2 : 3-dimethylquinoxaline 1 : 4-dioxide (4·1 g.), 2-amino-4-chloro-1 : 6-dimethylpyrimidinium iodide (Ainley *et al.*, *J.*, 1953, 59) (5·7 g.), water (115 c.c.) and 2N-hydrochloric acid (10 c.c.) were refluxed for 30 min., then cooled, and the *product* (6·75 g.) was collected. It crystallised from water in yellow prisms, decomp. *ca.* 240° (Found : C, 39·4; H, 4·85; N, 16·8; I, 25·35. $C_{16}H_{19}O_2N_6I,2H_2O$ requires C, 39·2; H, 4·75; N, 17·15; I, 25·9%).

*Reaction of* 2 : 3-*dimethylquinoxaline oxide with methyl iodide*. 2 : 3-Dimethylquinoxaline 1-oxide (2·1 g.), methyl iodide (4 g.), and methyl cyanide (20 c.c.) were refluxed overnight and then evaporated to dryness under reduced pressure. The residue was extracted three times

with boiling *cyclo*hexane to remove unchanged **2 : 3**-dimethylquinoxaline 1-oxide (*ca.* 1 g.) and was crystallised twice from methanol, giving **1 : 2 : 3**-*trimethylquinoxalinium tri-iodide* 4-*oxide* (*ca.* 100 mg.) as dark brown prisms, m. p. 144—145° (Found : C, 23·5; H, 2·2; N, 4·1; I, 66·5. $C_{11}H_{13}ON_2I_3$ requires C, 23·15; H, 2·3; N, 4·9; I, 66·8%).

Some of the work described in this paper is incorporated in B.P. 668,412.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, RESEARCH LABORATORIES,
HEXAGON HOUSE, MANCHESTER, 9. [*Received, May* 16*th*, 1953.]

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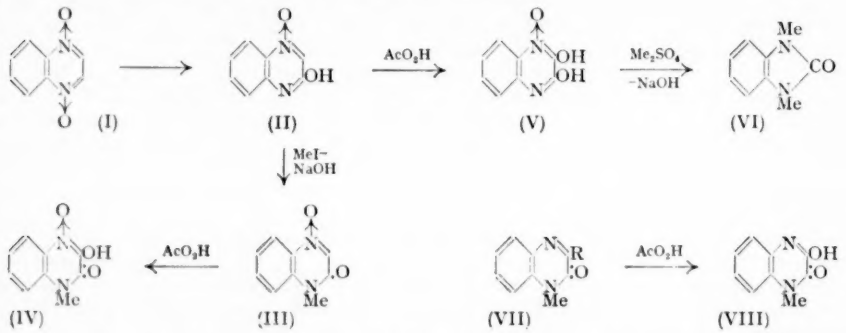
## 569. *Quinoxaline* N-*Oxides. Part III.* Photochemical Decomposition of Quinoxaline Mono- and Di-*N*-oxides.*

By JUSTUS K. LANDQUIST.

Photochemical decomposition of quinoxaline 1-oxide affords 2-hydroxyquinoxaline. Quinoxaline 1 : 4-dioxide undergoes rapid photochemical decomposition in dilute solution, the course of the reaction being influenced by the solvent. In dilute hydrochloric acid the product is a chloroquinoxaline mono-*N*-oxide, and in water or dilute sulphuric acid 2-hydroxyquinoxaline 4-oxide is formed. Some 1-methylquinoxal-2-one 4-oxides are described.

WHILE developing a spectrophotometric method for the determination of quinoxaline 1 : 4-dioxide (I) in biological materials Dr. A. Spinks (personal communication) found that the absorption spectrum of dilute solutions changed rapidly on exposure to light. At the same time it was found that the amœbicidal activity of solutions of (I) was lost on storage in clear glass bottles exposed to daylight or to ultra-violet light Decomposition of 0·05% solutions in a silica cell 15" from a Hanovia ultra-violet lamp was complete in 10—30 minutes, the rate of reaction and the spectrum of the end products varying with the solvent. Numerous other quinoxaline di-*N*-oxides were examined, and all showed about the same degree of photochemical instability. McIlwain (*J.*, 1943, 322) found that the production of a blue product from 2-methylquinoxaline 1 : 4-dioxide in alkaline solution was greatly accelerated by light.

Quinoxaline 1-oxide in aqueous solution undergoes a slower photochemical decomposition than (I); the product was identified as 2-hydroxyquinoxaline. Irradiation of (I) in dilute hydrochloric acid gives a compound $C_8H_5ON_2Cl$, whose absorption spectrum and other physical properties resemble those of quinoxaline 1-oxide. It is not identical with any of the chloroquinoxaline mono-*N*-oxides described in Part I (*J.*, 1953, 2816). On prolonged irradiation it undergoes further decomposition.

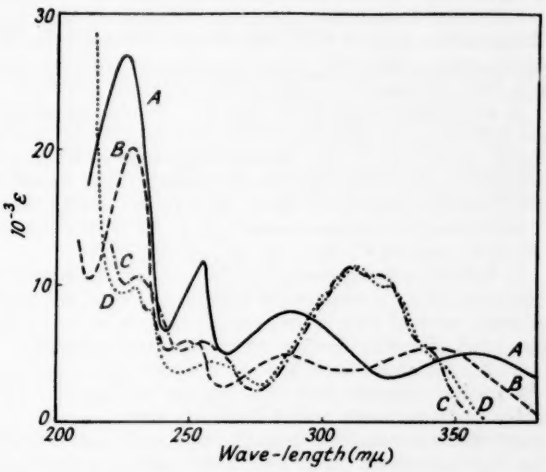



In chloroform and in aqueous alkali, (I) undergoes photochemical decomposition to end-products with indefinite absorption spectra which suggest complex mixtures, but in

* Part II, preceding paper.

water or dilute sulphuric acid a single compound, $C_8H_6O_2N_2$, m. p. 275°, with an absorption spectrum resembling that of 2-hydroxyquinoxaline, is obtained. This does not show the reactions of a hydroxamic acid, and it was shown to be 2-hydroxyquinoxaline 4-oxide (II) by the following reactions: methylation with methyl iodide and sodium hydroxide afforded a methyl derivative (III), m. p. 208—209°, which contained no methoxyl groups, and this on oxidation with peracetic acid gave 3-hydroxy-1-methylquinoxal-2-one 4-oxide (IV), identical with material obtained by cyclisation of nitrosomalonic bis-*N*-methylanilide and subsequent hydrolysis (Usherwood and Whiteley, *J.*, 1923, 1069). Peracetic acid oxidation of (II) gave 2 : 3-dihydroxyquinoxaline 4-oxide (V), the absorption spectrum of which resembled that of 2 : 3-dihydroxyquinoxaline, and this compound on treatment with methyl sulphate and sodium hydroxide was degraded and methylated to 1 : 3-dimethylbenziminazol-2-one (VI).

The methyl derivative (III) is 1-methylquinoxal-2-one 4-oxide, which Usherwood and Whiteley (*loc. cit.*) obtained from nitromalonic bis-*N*-methylanilide and described as melting




*Absorption spectra in* 0·1N-*hydrochloric acid.*
*A*, 2-*Hydroxyquinoxaline* 4-*oxide.*
*B*, 2-*Hydroxyquinoxaline.*
*C*, 2 : 3-*Dihydroxyquinoxaline* 4-*oxide.*
*D*, 2 : 3-*Dihydroxyquinoxaline.*

at 192—194°. Peracetic acid oxidation of 1-methylquinoxal-2-one (VII; R = H), and of methyl 1 : 2-dihydro-1-methyl-2-oxo-3-quinoxalinylacetate (VII; R = $CH_2 \cdot CO_2Me$) gave 3-hydroxy-1-methylquinoxal-2-one (VIII), but 1 : 3-dimethylquinoxal-2-one (VII; R = Me) on oxidation gave a small yield of 1 : 3-dimethylquinoxal-2-one 4-oxide. Methylation of ethyl 2-hydroxy-3-quinoxalinylacetate with methyl sulphate in alkaline solution gave (VII; R = $CH_2 \cdot CO_2Me$); the ethyl ester (VII; R = $CH_2 \cdot CO_2Et$) was prepared from *N*-methyl-*o*-phenylenediamine and ethyl ethoxalylacetate, and the acid obtained on hydrolysis of the ester was unstable, yielding (VII; R = Me) by decarboxylation at room temperature.

Some absorption spectra are shown in the Figure.

## Experimental

*Isolation of Irradiation Products.*—(*a*) Quinoxaline 1-oxide (0·5 g.) in water (100 c.c.) was irradiated by a Hanovia ultra-violet lamp for 14 days and then by daylight for an equal time. 2-Hydroxyquinoxaline (0·1 g.) crystallised out, and after extraction with dilute sodium hydroxide solution, treatment with carbon, reprecipitation, and crystallisation from ethanol, it melted at 262—264°, alone or admixed with an authentic specimen.

(*b*) Quinoxaline 1 : 4-dioxide (0·5 g.) in 0·5N-hydrochloric acid (50 c.c.) was irradiated by a Hanovia lamp until the absorption spectrum indicated that decomposition was complete (about 2 weeks). The filtered solution was concentrated under reduced pressure to about 5 c.c. and the crystalline solid (0·2 g.) collected, washed with water, dried, and extracted with

*cyclo*hexane, leaving a trace of high-melting solid, probably 2 : 3-dihydroxyquinoxaline (similar absorption spectrum). The *chloroquinoxaline 1-oxide* crystallised from *cyclo*hexane in long colourless needles, m. p. 114° (Found : C, 53·2; H, 2·6; N, 15·1; Cl, 19·9. $C_8H_5ON_2Cl$ requires C, 53·2; H, 2·8; N, 15·5; Cl, 19·65%).

(*c*) Quinoxaline 1 : 4-dioxide (7·5 g.) was dissolved in water (500 c.c.) by warming and the solution was left in full daylight (direct sunlight when possible) in a glass flask. The product began to separate after 2—3 hr., together with some quinoxaline 1 : 4-dioxide which was re-dissolved by warming. After 2 weeks the solid (3·0 g.) was collected, dissolved in dilute sodium hydroxide solution, clarified with carbon, and precipitated with acetic acid. *2-Hydroxyquinoxaline 4-oxide* crystallised from glacial acetic acid in buff prisms, m. p. 274—275° (Found : C, 59·0; H, 3·8; N, 17·6. $C_8H_6O_2N_2$ requires C, 59·3; H, 3·7; N, 17·3%).

*1-Methylquinoxal-2-one 4-Oxide.*—2-Hydroxyquinoxaline 4-oxide (2·0 g.), dissolved in 4% sodium hydroxide solution (30 c.c.) and methanol (30 c.c.), was shaken with methyl iodide (6 c.c.) for 5 hr., and the product (1·1 g.) was collected next day and crystallised from benzene, forming pale buff needles, m. p. 208—209° (Found : C, 61·4; H, 4·5; N, 16·2; OMe, 0. Calc. for $C_9H_8O_2N_2$ : C, 61·3; H, 4·55; N, 15·9%).

*3-Hydroxy-1-methylquinoxal-2-one 4-Oxide.*—1-Methylquinoxal-2-one 4-oxide (0·5 g.) and 1·2M-peracetic acid (5 c.c.) were heated overnight at 50°. The product crystallised out in needles, m. p. 253—255° alone or admixed with 3-hydroxy-1-methylquinoxal-2-one 4-oxide, m. p. 257°, prepared by Usherwood and Whiteley's method.

*2 : 3-Dihydroxyquinoxaline 4-Oxide.*—2-Hydroxyquinoxaline 4-oxide (2·5 g.), glacial acetic acid (100 c.c.) and 30% hydrogen peroxide (50 c.c.) were heated at 50° overnight, cooled, and diluted with water. The product separated in white globular aggregates of crystals which changed to pale brown rhomboidal tablets of the *hydrate* (Found : C, 49·0; H, 3·9; N, 14·4. $C_8H_6O_3N_2,H_2O$ requires C, 49·0; H, 4·1; N, 14·3%), which at 100° fell to a white powder of *2 : 3-dihydroxyquinoxaline 4-oxide*, m. p. 290° (decomp.) (Found : C, 53·5; H, 3·2; N, 15·4. $C_8H_6O_3N_2$ requires C, 53·9; H, 3·4; N, 15·7%).

*1 : 3-Dimethylbenziminazol-2-one.*—(*a*) Benziminazolone (1 g.), dissolved in 2N-sodium hydroxide (10 c.c.), was shaken with methyl sulphate (3 c.c.) for 2—3 hr., and the product was collected, washed with a little cold water, dried, and crystallised from light petroleum (b. p. 100—120°), forming needles which gradually changed to shorter prisms, m. p. 107—108°. (*b*) 2 : 3-Dihydroxyquinoxaline 4-oxide (1·0 g.) in 2N-sodium hydroxide (15 c.c.) was treated with methyl sulphate (2·5 c.c.), further additions of methyl sulphate (1·5 c.c.) and sodium hydroxide being made after 3 days and after 1 week. On long storage stout needles of 1 : 3-dimethylbenziminazolone (0·45 g.) separated and, crystallised from water (carbon) and then from light petroleum (b. p. 100—120°), had m. p. and mixed m. p. 107° (Found : C, 66·4; H, 6·3; N, 17·2. Calc. for $C_9H_{10}ON_2$ : C, 66·6; H, 6·2; N, 16·8%).

*Methyl 1 : 2-Dihydro-1-methyl-2-oxo-3-quinoxalinylacetate.*—Crude ethyl 2-hydroxy-3-quinoxalinylacetate (29 g.) was dissolved in 1·5N-sodium hydroxide (200 c.c.) and methanol (50 c.c.) and shaken at 0—5° with methyl sulphate (30 c.c.). The *product* (7·0 g.; m. p. 155—157°) crystallised slowly, and formed orange needles, m. p. 164—166°, from ethanol (Found : C, 61·7; H, 5·2; N, 12·0. $C_{12}H_{12}O_3N_2$ requires C, 62·05; H, 5·2; N, 12·1%).

*Ethyl 1 : 2-Dihydro-1-methyl-2-oxo-3-quinoxalinylacetate.*—*N*-Methyl-*o*-phenylenediamine (2·25 g.), ethyl ethoxalylacetate sodium salt (4·5 g.), and 10% acetic acid (50 c.c.) were heated on the steam-bath for 30 min. The oil which separated rapidly and then hardened was collected when cold, washed with water and crystallised from ethanol (carbon), giving *ethyl 1 : 2-dihydro-1-methyl-2-oxo-3-quinoxalylacetate* as yellow platelets or hair-like needles, m. p. 140—142° (Found : C, 63·1; H, 5·4; N, 11·6. $C_{13}H_{14}O_3N_2$ requires C, 63·4; H, 5·7; N, 11·4%).

*Hydrolysis.* The foregoing ester (0·9 g.) was boiled under reflux for 30 min. with 2N-sodium hydroxide, and the warm solution was acidified with acetic acid. There was a prolonged effervescence, and 1 : 3-dimethylquinoxal-2-one crystallised slowly (m. p. and mixed m. p. 86—87°).

*1 : 3-Dimethylquinoxal-2-one 4-Oxide.*—1 : 3-Dimethylquinoxal-2-one (17·6 g.) and 1·2M-peracetic acid (280 c.c.) were heated at 50° overnight, evaporated under reduced pressure to 60—70 c.c., and neutralised with 40% sodium hydroxide solution and ice. The aqueous layer was decanted from tar and extracted with chloroform, and the extract dried ($Na_2SO_4$) and evaporated. Four crystallisations of the residue from ethanol (carbon) gave *1 : 3-dimethylquinoxal-2-one 4-oxide* (0·3 g.) as faintly pink needles, m. p. 200—202° (Found : C, 63·0; H, 5·25; N, 14·4. $C_{10}H_{10}O_2N_2$ requires C, 63·15; H, 5·25; N, 14·75%). A further 0·25 g. was recovered from the tar by repeated crystallisation from benzene and then ethanol.

*Other Oxidations.*—Peracetic acid, heated overnight at 50° with 1-methylquinoxal-2-one or methyl 1 : 2-dihydro-1-methyl-2-oxo-3-quinoxalinylacetate, gave 30—50% yields of 1-methyl-3-hydroxyquinoxal-2-one, m. p. and mixed m. p. 284—286°.

I am indebted to Dr. A. Spinks for measurements of absorption spectra, and for observations on the rate of photochemical decomposition of the substances examined.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION,
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9. [*Received, May 16th*, 1953.]

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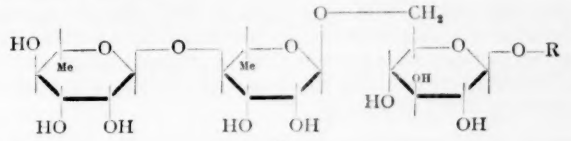
# NOTES.

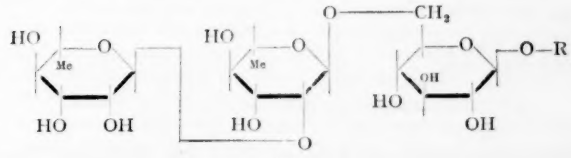
## 570. Solanum *Alkaloids. Part XI.* The Mode of Linkages in the Trisaccharide Moiety of Solamargine.*

By LINDSAY H. BRIGGS and E. G. BROOKER.

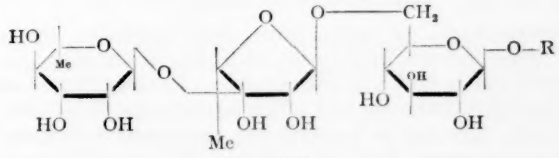
IN Part VIII (*J.*, 1952, 3587) it was shown that solamargine from *Solanum marginatum* was a new trisaccharide derivative of solasodine of the structure, rhamnose-rhamnose-glucose-solasodine, with the trisaccharide joined to solasodine through the hydroxyl group at $C_{(3)}$. Solamargine exhibits no reducing properties, so that the three sugars are all joined through their potential aldehyde groups. Glucose is joined to solasodine through a β-linkage and from the ease of hydrolysis with 2% mineral acids the rhamnose units are also most probably similarly joined.



(I)



(II)



(III)

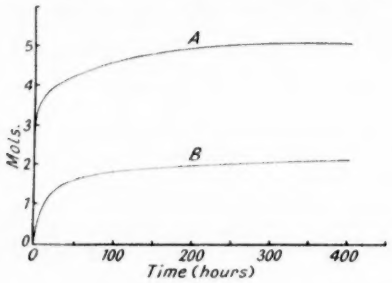
Quantitative oxidation of solamargine with periodate at 25°, illustrated in the Figure, showed that 5 mols. of periodate were consumed and 2 mols. of formic acid produced. Of the 96 possible structures for the trisaccharide moiety, including both pyranose and furanose forms of each sugar (but excluding the posibility of α- or β-linkages), only the three annexed structures (R = solasodine) could give the results actually obtained. Structures (I) and (III) cannot be distinguished by the rate of oxidation or by the identification of the hydroxy-acids formed by further oxidation and hydrolysis of the initial hexa-aldehyde

* Part X, *J.*, 1953, 2809.

produced by periodate oxidation. Also, they cannot be distinguished by methylation, hydrolysis, and identification of the methylated sugars, since the 2 : 3-di-*O*-methylrhamnose formed could exist in either of the theoretically interconvertible pyranose and furanose forms. However, it is most unlikely that rhamnose would occur in furanose form and even more unlikely that one molecule should exist in pyranose form and the other in furanose form. For these reasons (III) can be excluded.

Structures (I) and (II) could be distinguished by methylation. However, 1 : 2′-linkages in naturally occurring sugars are extremely rare (see Part X), so we prefer (I). This trisaccharide moiety is also that preferred for solanine and solasonine (Part X).

The same combination of sugars (two mols. of rhamnose and one of glucose) occurs in only one other glycoside, convallamarin (Voss and Vogt, *Ber.*, 1936, **69**, 2333), but the order of components and the nature of the linkages have not been determined.




*A*, *Periodate consumed.*
*B*, *Formic acid produced.*

*Experimental.—Periodate oxidation of solamargine at 25°.* By the procedure outlined in Part X (*loc. cit.*) anhydrous solamargine (0·5281 g.) was dissolved in 0·0243N-formic acid (75 c.c. 3 mols.), 0·0364N-sodium metaperiodate solution (150 c.c., 9 mols.) added, and the volume made up to 500 c.c. All solutions before mixing had been held at 25°. The final solution was held at 25° and aliquots were examined at intervals.

We are indebted to the Chemical Society and the Research Grants Committee of the University of New Zealand for continued grants and one of us (E. G. B.) for a University Research Fellowship.

Auckland University College,
Auckland, New Zealand. [*Received, April 20th*, 1953.]

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## 571. α-*Benzylidenepropiophenone and its Halogen Derivatives.*

By Robert D. Abell.

α-Benzylidenepropiophenone, prepared, with other products, by condensation of benzaldehyde with propiophenone in presence of hydrogen chloride (*J.*, 1901, **79**, 929), requires chemical treatment to render it chlorine-free. Kohler (*Amer. Chem. J.*, 1904, **31**, 642) obtained an intermediate chloro-ketone which he decomposed by heat. Condensation in presence of hydrogen chloride or bromide has now yielded β-chloro- and β-bromo-α-methyl-β-phenylpropiophenone, Hal·CHPh·CHMe·COPh, each in two isomeric forms, which differ slightly in their reactions.

*Experimental.—α-Benzylidenepropiophenone* (cf. Abell, *loc. cit.*). The dark product (A, see below), obtained by saturating a mixture of benzaldehyde (53 g.) and propiophenone (67 g.) with hydrogen chloride and storage of the mixture for 2 days, was slowly heated to 200° and kept at that temperature for some time. To obtain chlorine-free material, this product must then be boiled or steam-distilled with aqueous alkali for 10—12 hr. or boiled with alcoholic potassium acetate (20 g.) for 5—6 hr. Pouring the whole into water and removal of alcohol and unchanged reactants in steam gave a very dark, chlorine-free oil. When washed in light petroleum, dried, and distilled this afforded α-benzylidenepropiophenone as a yellow oil, b. p. 210—212°/20 mm.

Its phenylhydrazone formed lemon-yellow crystals, m. p. 128°. Kohler's record (*loc. cit.*) of m. p. 131° could not be repeated in many experiments.

*β-Chloro-α-methyl-β-phenylpropiophenone.* (*a*) To a solution of benzaldehyde (20 g.) in carbon disulphide (100 c.c.), saturated with hydrogen chloride, propiophenone (40 g.) was carefully added. After storage for several days, evaporation gave a dark oil which was dissolved in light petroleum (b. p. 40—60°), washed with water and then aqueous sodium carbonate, thoroughly dried ($CaCl_2$ or $Na_2SO_4$), and concentrated by evaporation (there is no decomposition if water is absent) until crystallisation occurred on cooling and scratching of a portion. Slow cooling of the bulk then gave *β-chloro-α-methyl-β-phenylpropiophenone* as rounded tufts of prisms, m. p. 79° (Found : Cl, 13·7. $C_{16}H_{15}OCl$ requires Cl, 13·7%), usually accompanied by the *isomer* in the form of large dense prisms, m. p. 68° (Found : Cl, 13·7%). If the second isomer does not crystallise spontaneously, it may be obtained from the mother-liquor on decantation. Mixtures of the two forms are readily separated by floating off the lighter form of m. p. 79°. Purification by crystallisation from light petroleum (or from alcohol, but less well owing to slow hydrolysis by water present) gave materials of the m. p.s quoted above. The whole product may, by repetition of these processes, be separated into the above-mentioned two forms, except for a small amount of readily soluble oil which yields the unsaturated ketone.

(*b*) The dark oil A (see p. 2834) similarly gave both isomers on treatment with light petroleum.

(*c*) The crystals of m. p. 79° were unchanged when heated at 80° for 1 hr. but decomposed at slightly above this temperature; those of m. p. 68° decomposed only at 200° (stable for 1 hr. at 95°).

The form of m. p. 79° gave 93·5% of its chlorine in the ionic form when boiled for 1 hr. with alcoholic potassium acetate (excess); with the isomer of m. p. 68° there was only 78·2% reaction on such treatment. In both cases α-benzylidenepropiophenone was regenerated.

The isomer of m. p. 79° (2·0 g.), when boiled for 3 hr. with phenylhydrazine (2 g.) in alcohol (55 c.c.), gave a dark, halogen-free viscous oil, stable at room temp. and giving Knorr's pyrazolone reaction. The isomer of m. p. 68°, on similar treatment, gave *4-methyl-1 : 3 : 5-triphenylpyrazoline* as plates, m. p. 143° (Knorr's pyrazolone reaction positive) (Found : N, 8·9. $C_{22}H_{20}N_2$ requires N, 9·0%).

*β-Bromo-α-methyl-β-phenylpropiophenone.* (i) Passage of hydrogen bromide into a solution of propiophenone (67 g.) and benzaldehyde (53 g.) in carbon disulphide (100 c.c.) caused evolution of heat and separation of water. After 2 days the product was recovered. It partly crystallised. Addition of light petroleum gave a large yield of crystals, m. p. 93°. The mother-liquors and washings gave material, m. p. 80°, of which more was obtained on evaporation to half-volume. Further concentration and saturation with hydrogen bromide yielded further amounts of both isomers. The marked difference in solubility in light petroleum permitted finally complete separation of the *β-bromo-α-methyl-β-phenylpropiophenone* into the less soluble needles, m. p. 93° (Found : Br, 26·5. $C_{16}H_{15}OBr$ requires Br, 26·4%), and more soluble prisms, m. p. 80° (Found : Br, 26·5%). A small residue of dark oil yielded the unsaturated ketone.

(ii) A solution of α-benzylidenepropiophenone (50 g.) in carbon disulphide (100 c.c.), when saturated with hydrogen bromide, became dark and warm. After 24 hr., more carbon disulphide (100 c.c.) was added and the product isolated. This yielded the isomers, m. p. 93° (2 parts) and 80° (1 part). A similar experiment conducted in artificial light, gave only the isomer of m. p. 93°.

(iii) Reaction as in (*a*) but with hydrogen bromide in place of hydrogen chloride, and working up as in (i) gave only the isomer of m. p. 93° (perhaps owing to unsuitable lighting).

(iv) The isomer of m. p. 93° is dimorphous. A solution in hot carbon disulphide deposited long, flattened prisms resembling in form the isomer of m. p. 80° but melting at 93°. When kept in contact with the solution these prisms were replaced by the usual needles (m. p. and mixed m. p. 93°).

(v) The isomer of m. p. 93° decomposes at about 145°, the other isomer decomposes slightly above its m. p. (80°).

(vi) The isomer of m. p. 93° gave 98·8% of its bromine in the ionic form when boiled with alcoholic potassium acetate (excess) for 1 hour.

It did not react with hydroxylamine in alcohol when the solution was acid or neutral to methyl-orange (pH 5), but in solution just alkaline to phenolphthalein (pH 9) gave a halogen-free *substance* as prisms which soften at about 145° and are completely molten at 161° (unchanged on recrystallisation) (Found : 5·85. $C_{16}H_{15}ON$ requires N, 5·9%). This is also obtained when α-benzylidenepropiophenone is treated with hydroxylamine in acid solution and may be the oxime or 4-methyl-3 : 5-diphenyl*iso*oxazoline.

With hydrazine hydrate the isomer of m. p. 93° gave an alcohol-soluble oil and a small amount of sparingly soluble hexagonal plates (? the hydrazone), m. p. 220—221°, which contain bromine and do not give Knorr's pyrazolone test.

The same isomer (3·0 g.) and phenylhydrazine (2·2 g.), heated in alcohol (25 c.c.) for 1 hr., gave quantitatively 4-methyl-1 : 3 : 5-triphenylpyrazoline, m. p. 143° (Found : N, 8·9%).

TECHNICAL COLLEGE, BRADFORD. [*Received, January 5th,* 1953.]

## 572. *Electric Moments and Intermolecular Hydrogen Bonds of Cyclic Amides and Oxazolidones : A Correction.*

By ERNST FISCHER.

RECENTLY (Fischer, *J.*, 1952, 4525) an attempt was made to estimate the contribution of bipolar mesomers to the structure of pyrrolid-2-one and of oxazolid-2-one. The author is indebted to Professor W. D. Kumler for pointing out an error in the " theoretical " moments then used, due to assignment of an incorrect value to the angle between the moment of the N–H bond and the resultant moment of the rest of the molecule.

In the pyrrolidone this angle plausibly has a value of between 110° (pyramidal arrangement of the three nitrogen valencies being accepted) and 124·5°, the H atom being assumed to lie in the plane of the ring. An intermediate value of 116° leads to a " theoretical" moment of *ca.* 3·0 D, without account being taken of mutual induction of the polar groups within the molecule. In the oxazolidone the corresponding figures are 102°, 104°, 103°, and 3·55 D. Combination of these " theoretical " moments with the experimental moments of 4·2 D for pyrrolidone and 5·1 D for oxazolidone leads to calculated contributions of bipolar mesomers (assumed to have a moment of 11 D) of 15% and 21%, respectively, and not 5% and 16% as reported previously. The main uncertainties concern the neglect of mutual induction within the molecules, as well as possible errors in the moment of the bipolar mesomer, in the valency angle mentioned above, and in the " experimental " moment of pyrrolid-2-one.

In the original communication attention was drawn to the parallelism between the contribution of bipolar mesomers and the tendency to association in benzene solutions. The present figures show this parallelism to be less pronounced.

WEIZMANN INSTITUTE OF SCIENCE,
REHOVOT, ISRAEL. [*Received, April 2nd,* 1953].

## 573. *Free-radical Formation in Oxidations by Manganic Pyrophosphate.*

By ALAN Y. DRUMMOND and WILLIAM A. WATERS.

MANGANIC PYROPHOSPHATE was previously shown by us (*J.*, 1953, 435) to be a selective oxidising agent which slowly attacks most water-soluble aldehydes and ketones, 1 : 2-glycols α-hydroxy-acids, and a few other compounds, but not monohydric alcohols or olefins. Kinetic studies on which we are now engaged indicate that the exact courses of these oxidations depend very much upon the structural type of the organic compound involved. The following evidence indicates however that in each case the initial attack on the organic molecule, which may be represented as

$$(a)\ \mathrm{R{-}H} + \mathrm{Mn^{3+}} \longrightarrow \mathrm{R\cdot} + \mathrm{Mn^{2+}} + \mathrm{H^{+}}$$

leads to the formation of an *active* free radical.

1. *Catalysis of Vinyl Polymerisation.*—Manganic pyrophosphate solutions do not attack olefins. Consequently aqueous solutions of vinyl cyanide and of methyl methacrylate do not, in the absence of air, polymerise for a long time when added to neutral or acidified manganic pyrophosphate solutions; but if an oxidisable organic compound is added then the deposition of insoluble polymer is soon evident, even when the oxidation of the organic compound is quite slow. Decisive positive results have been obtained for the oxidations of the following compounds :

1 : 2-*Glycols.* Vinyl cyanide polymerisation is induced in the cold by the oxidation of

butane-1 : 2-diol, butane-2 : 3-diol, pinacol, erythritol, mannitol, or sorbitol. Of these only butane-2 : 3-diol and pinacol readily induced methyl methacrylate polymerisation, though with the others polymerisation was evident after 5 hours. Ethylene glycol and glycerol oxidised too slowly to induce visible polymerisation.

*Aldehydes and ketones.* With both monomers, positive results have been obtained for the oxidations of acetaldehyde, propaldehyde, butyraldehyde, acetone, ethyl methyl ketone, *cyclo*pentanone, 3-methyl*cyclo*pentanone, *cyclo*hexanone, and 4-methyl*cyclo*hexanone.

*Carboxylic acids.* Oxidation of oxalic, glycollic, lactic, tartronic, tartaric, malic, citric, or malonic acid induced polymerisations of both monomers. With oxalic and tartronic acids the induced polymerisation occurred rapidly; with glycollic acid the induced polymerisation of methyl methacrylate was evident only after 5 hours.

*Phenols.* Phenols, being oxidised, could not be tested in this way since they immediately gave dark precipitates.

To obviate effects due to oxygen, all tests were carried out in Thunberg tubes. Constant volumes of monomer, manganic pyrophosphate solution (*loc. cit.*), and dilute sulphuric acid were placed in the main Thunberg tube and about $1{\cdot}2 \times 10^{-3}$ mole of substrate in the side-tube. After evacuation the contents of the tubes were mixed and then kept at room temperature until precipitation was evident.

2. *Reduction of Mercuric Chloride.*—Active free radicals with $E_{(-e)}$ below *ca.* +0·6 v are capable of reducing mercuric chloride to mercurous chloride (Merz and Waters, *J.*, 1949, S 15; Mackinnon and Waters, *J.*, 1953, 323). Though manganic pyrophosphate has a much higher redox potential the insolubility of mercurous chloride favours the occurrence of some reduction (*b*) in competition with further oxidation by the manganic salt (*c*).

$$(b)\ R\cdot + Hg^{2+} \longrightarrow R^{+} + Hg^{+}$$
$$(c)\ R\cdot + Mn^{3+} \longrightarrow R^{+} + Mn^{2+}$$

Though the reduction of mercuric chloride can be effected only by a limited group of free radicals, we have found that each one of the substrates listed in section (1) above does bring about some deposition of mercurous chloride when added to manganic pyrophosphate–mercuric chloride solutions at pH 0·8 and kept at 40° for a few hours. It is to be noted that this list includes compounds which do not give similar induced reductions when treated with Fenton's reagent, *e.g.*, acetone and pinacol.

In the case of oxalic acid it was found that copious precipitation of mercuric chloride results from the addition of only a few drops of manganic pyrophosphate solution to an aqueous oxalic acid–mercuric chloride mixture. Here the reduction $Mn^{3+} + (C_2O_4)^{2-} \longrightarrow Mn^{2+} + \cdot O_2C\cdot CO_2^{-}$ serves to catalyse the known oxalic acid–mercuric chloride chain reaction (Dhar, *J.*, 1917, **111**, 690; Cartledge, *J. Amer. Chem. Soc.*, 1941, **63**, 906; Weiss, *Discuss. Faraday Soc.*, 1947, **2**, 188). Dhar had reported some similar induced reductions of mercuric chloride during oxidations of α-hydroxy-acids by potassium permanganate.

One of us (A. Y. D.) thanks the D.S.I.R. for a Maintenance Grant.

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, March 16th,* 1953.]

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## 574. *Observations on Exaltations of Molecular Refractions.*

By ERNST D. BERGMANN and ERNST FISCHER.

EVERARD, KUMAR, and SUTTON (*J.*, 1952, 2807) and Everard and Sutton (*J.*, 1952, 2816, 2817, 2818, 2821, 2836) studied the influence of conjugation on the molecular refraction and, in particular, on the distortion polarisation of compounds of the diphenyl, styrene, stilbene, and 1 : 4-diphenylbutadiene series (cf. Weizmann, *Trans. Faraday Soc.*, 1949, **36**, 928; Calvin and Alter, *J. Chem. Phys.*, 1951, **19**, 765; Curran and Palermiti, *J. Amer. Chem. Soc.*, 1951, **73**, 3733); an analogous study of substances of the above type and also of abnormal molecular refractions of coloured hydrocarbons has been carried out by Berg-

mann, Fischer, and Jaffe (*J. Amer. Chem. Soc.*, 1953, **75**, in the press). Additional data, related to some colourless or almost colourless substances, are reported in Table 1.

| | $(R_D)_{calc.}$ (c.c.) | $(R_D)_{obs.}$ (c.c.) | Absorption max. (Å) (log $E_m$) |
|---|---|---|---|
| 4-Methoxystilbene ..... | 67·2 * | 68·5 ± 1·5 | 3150; 3250 [a] |
| *p*-Methoxybenzylideneaniline | 64·5 | 71·0 ± 0·3 | 2230 (4·22); 2850 (4·24) (Fig. 1)[f] |
| Sorbic acid ..... | 31·2 | 34·0 ± 0·5 | 2540 (in alcohol) [b] |
| Triphenylene ..... | 83·0 | 81·5 ± 0·8 | 2500; 2580; 2740; 2840; 3000; 3220; 3280; 3340 [c] |
| Acenaphthene ..... | 51·5 | 52·0 ± 0·5 | 2470; 2670; 2780; 2810; 2850; 2890; 2920; 2960; 3000; 3040; 3080; 3130; 3170; 3220 [d] |
| 3 : 4-Benzophenanthrene ..... | 83·0 | 83·5 ± 1 | 2180; 2290; 2620; 2720; 2810; 2950; 3030; 3150; 3250; 3540; 3710 [e] |
| Tetrabenzonaphthalene ..... | 113·0 | 122 ± 1 | 2320; 2680; 2870; 3010; 3380; 3500 [g] |

* Based on $(R_D)_{obs.}$ 36·5 for styrene (Everard *et al.*, *loc. cit.*), which gives $R_D$ 60·8 for stilbene. If the observed values for *cis*- (61·8) or *trans*-stilbene (65·6) (Everard *et al.*) are used, the above figure would be correspondingly higher.

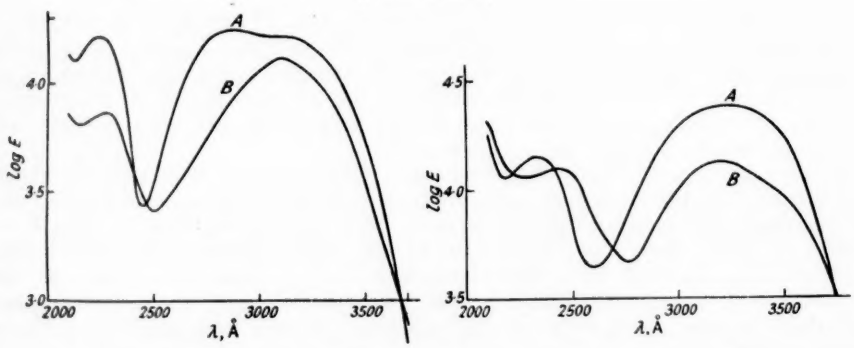
[a] Calvin and Alter, *loc. cit.*; cf. Ley, *Z. physikal. Chem.*, 1920, **94**, 405. [b] Hausser, Kuhn, Smakula, and Hoffer, *ibid.*, 1935, **29**, *B*, 371. [c] Clar and Lombardi, *Ber.*, 1932, **65**, 1411; Mohler and Sorge, *Helv. Chim. Acta*, 1939, **22**, 229. [d] Titeica, *Ann. Comb. liq.*, 1962, **11**, 445; *Chem. Abs.*, 1936, **30**, 6644; Seshan, *Proc. Indian Acad. Sci.*, 1936, **3**, 148. [e] Mayneord and Roe, *Proc. Roy. Soc.*, 1937, *A*, **158**, 634. [f] See Witkop, Patrick, and Kissman, *Ber.*, 1952, **85**, 949. [g] Bergmann, Fischer, and Jaffe, *loc. cit.*

4-Methoxy-groups in systems of the stilbene type should exert a conjugation effect similar to that of amino-groups. In distinction to 4-aminostilbene and its *N*-dimethyl

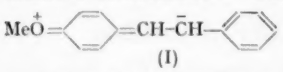
FIG. 1. p-*Methoxybenzylidene aniline* (*A*) *and* ω-*nitrosystrene* (*B*).

FIG. 2. 4-*Aminostilbene* (*A*) *and* 4-*dimethylaminostilbene* (*B*).

(*All in ethanol.*)




derivative (reported by Everard, Kumar, and Sutton, *loc. cit.*) *p*-methoxystilbene shows practically no effect of this kind; in *p*-methoxybenzylideneaniline (*p*-MeO·$C_6H_4$·CH:NPh) it is more pronounced. In this respect, Everard, Kumar, and Sutton's observation is of interest that the conjugation effect is much smaller for 4-methoxy- than for 4-dimethylamino-4'-nitrostilbene. This difference has also been noted by Bergmann and Weizmann (*Chem. Reviews*, 1942, **29**, 553); the methoxy-group has a smaller tendency to form structures such as (I) than the amino-group.



(I)

Unlike the coloured polycyclic hydrocarbons previously studied, the colourless compounds triphenylene, acenaphthene, and 3 : 4-benzophenanthrene show no exaltation of the molecular refraction, in spite of the extended conjugated systems. Tetrabenzonaphthalene shows a somewhat anomalous behaviour; this may be ascribed to the abnormal structure of this hydrocarbon, in which some of the carbon–carbon bonds appear to be non-aromatic, according to the *X*-ray analysis of the crystal structure (" intramolecular overcrowding ") (G. Schmidt, personal communication). An open-chain analogue, sorbic acid, shows a slight exaltation of the molecular refraction.

As well as the molecular refractions, the absorption spectra of the above compounds have been measured. Those which have not been reported before are reproduced here. They may be of interest for a theoretical evaluation of the reported exaltations of the molecular refractions (see Sörensen, *Annalen*, 1940, **546**, 58).

*Experimental.*—The following materials were used. 4-Methoxystilbene, m. p. 136° (from *iso*propyl alcohol) (Orékhoff and Tiffeneau, *Bull. Soc. chim.*, 1925, **37**, 1410). *p*-Methoxybenzylideneaniline, m. p. 61—62° (from alcohol) (Knoevenagel, *Ber.*, 1898, **31**, 2606). Sorbic acid (commercial product, recrystallised from aqueous alcohol), m. p. 134. ω-Nitrostyrene, m. p. 60° (from methanol) (*Org. Synth.*, Coll. Vol. I, 1934, p. 413). Triphenylene, m. p. 198° (from *iso*propyl alcohol) (E. Bergmann, Fischer, and B. Pullman, *J. Chim. phys.*, 1931, **48**, 356). Acenaphthene (commercial product, purified *via* the picrate and recrystallised from alcohol), m. p. 95°. 3 : 4-Benzophenanthrene, m. p. 68° (from alcohol) (Szmuszkovicz and Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 566). Tetrabenzonaphthalene, m. p. 218° (from toluene) (E. Bergmann, Fischer, and Pullman, *loc. cit.*). 4-Aminostilbene, m. p. 152° (from 80% methanol) (Pfeiffer and Sergiewskaja, *Ber.*, 1911, **44**, 1110). 4-Dimethylaminostilbene, m. p. 147° (from *iso*propyl alcohol) (Dey and Row, *J. Indian Chem. Soc.*, 1925, **1**, 285).

The method used for the determination of the molecular refraction has been described elsewhere (E. Bergmann, Fischer, and Jaffe, *loc. cit.*). The Table contains the molecular refractions, calculated from bond equivalents $(R_D)_{calc.}$ (Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 926), the observed value $(R_D)_{obs.}$ and the absorption bands.

For the absorption spectra, the authors are indebted to Miss Hanna Weiler.

Scientific Department, Israeli Ministry of Defence, Tel-Aviv.
Weizmann Institute of Science, Rehovoth. [*Received, January 30th*, 1953.]

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## 575. *The Vapour Pressure and Improved Preparation of Methaneselenol.*

By G. E. Coates.

Methaneselenol ($CH_3$·SeH), which was required for some experiments with trimethylgallium (Coates and Hayter, *J.*, 1953, 2519), is described by Baroni (*Atti Accad. Lincei*, 1930, **12**, 234), who prepared it from sodium hydrogen selenide and methyl iodide and gave its b. p. as 12°/758 mm. The reduction of dimethyl diselenide (Bird and Challenger, *J.*, 1942, 570) by sodium in liquid ammonia affords a more convenient preparative method.

The vapour pressure of methaneselenol, measured from −45° to +15°, is given by the equation $\log_{10}p = 6{\cdot}9500 - 1060/(t + 235)$ (where $p$ is measured in mm. and $t$ in degrees c). The average deviation of the pressures measured at 24 temperatures in this range from those calculated with the above equation is 0·8 mm. The b. p. is 25·5°. The latent heat of vaporisation is 6·20 ± 0·04 kcals./mole, the method of computation given by Thompson (*Chem. Reviews*, 1946, **38**, 1) being used with 228° c and 60 atm. as the critical temperature and pressure (values estimated by comparison with substances of similar constitution). The Trouton constant is thus 20·8. The latent heat of vaporisation is 6·48 kcal./mole, measured from the slope of the high-temperature (5—15°) part of the log $p/T^{-1}$ graph, no corrections being made for deviations from perfect-gas laws.

*Experimental.*—Dimethyl diselenide (19 g., 0·1 mole) and sodium (4·6 g., 0·2 g.-atom) were added alternately to boiling liquid ammonia (150 c.c.). Ammonia was allowed to boil away from the resulting reddish-orange solution, which was protected from the atmosphere. Dilute sulphuric acid was slowly added to the solid residue, and the evolved gas was carried in a current of nitrogen through two drying tubes ($CaCl_2$) and condensed in a trap cooled in liquid oxygen. The product was transferred to a vacuum apparatus and was purified by fractional distillation. The only impurity detected was a little hydrogen selenide. The yield was nearly quantitative. The smell of methaneselenol is strong but not persistent.

The University, Bristol. [*Received, March 10th*, 1953.]

# OBITUARY NOTICE.

## CHAIM WEIZMANN.

### 1874—1952.

On November 9th, 1952, Dr. Chaim Weizmann, distinguished chemist and first President of the State of Israel, died after a long illness at his home in Rehovoth.

Born on November 27th, 1874, in Motol in Czarist Russia, in the pale of Jewish settlement, Weizmann was a representative of that gifted type of Russian Jew who succeeded in the synthesis of the two antitheses, traditional Jewish culture and modern Western civilisation. Already in his youth, he joined the Zionist movement and rose quickly from the ranks to undisputed leadership. His thirst for knowledge, his interest in natural science which also had its roots in his school days, led Weizmann to the study of chemistry, and his achievements in this field were no mean ones. These two different directions of human endeavour, however, did not appear to be divergent in Weizmann's life; to him work in his profession was but one of the means of rebuilding of the Promised Land, and all his life he emphasised the role science would have to play in the State of Israel. Thus, he was the prime mover in the establishment of the Hebrew University, of the Hebrew Technical Institute of Haifa, and of the Daniel Sieff Research Institute, later enlarged into the Weizmann Institute of Science, at Rehovoth.

After having enjoyed the education traditional in Russian Jewry, Weizmann was sent in his 12th year to a Russian school (in Pinsk), at that time a somewhat unusual career for a Jewish youth. In his autobiography (" Trial and Error "), he describes the foundations his science teacher laid there for his later career. The *numerus clausus* at Russian Universities forced him, after having finished school, to turn westwards for further study. After a short sojourn at the University of Darmstadt, he enrolled in 1895 at the Technische Hochschule in Berlin-Charlottenburg, where at that time Liebermann was engaged with his pupils, notably Bistrzycki, in his classical studies in the polycyclic series. Weizmann followed Bistrzycki to Fribourg (Switzerland), where in 1900 he was awarded the degree of doctor *summa cum laude*. This rare distinction brought him an appointment as Privatdozent at the University of Geneva under Graebe who also recommended him to William Henry Perkin at Manchester University, when Weizmann, in 1904, decided to continue his work in England.

Weizmann's relation to England can only be described by the word " Wahlverwandtschaft," coined by Goethe. Undoubtedly, the period at Manchester was the happiest and scientifically the most creative in his life; it was there that he married Vera Chatzman, like him of Jewish-Russian origin. Of their two sons, one was killed on active service during the Second World War.

The faculty at Manchester was then adorned by some of the Immortals of British science; Weizmann was soon accepted into their community, and only the First World War severed this happy connection. It was one of the discoveries made at Manchester, that of a bacterium fermenting carbohydrates to yield acetone and butyl alcohol, which became of importance to the war effort and made it necessary for Weizmann—following an invitation by Lloyd George, then Head of the Ministry of Munitions, and Mr. Churchill, then First Lord of the Admiralty—to move to London. There, at the Lister Institute, and at the Admiralty Cordite Factory near Poole, the discovery was transformed into a technical process. It may be interesting to reflect that the " Weizmann fermentation " is but a further step on a road opened by another Manchester scholar, Arthur Harden, with his studies on the biochemistry of yeast fermentation.

The end of the war brought with it the Balfour Declaration and thus for Weizmann a measure of political responsibility which led to an interruption of his research until 1931, when his longing for scientific work became so overwhelming that he established a private laboratory at Featherstone Buildings, near High Holborn, in London. Here he took up some of his old subjects and initiated some new ones; at the same time, the Featherstone Laboratories became the planning centre for the Institute of Chemical Research which Weizmann established at Rehovoth and which bears the name of Daniel Sieff, son of one of Weizmann's closest friends and collaborators.

From April 4th, 1934, the day on which the new Institute was inaugurated, until the outbreak of the Second World War, Weizmann divided his time between the Institute in Palestine and the Featherstone Laboratories (which were destroyed by a German bomb early in the last

war). In 1939, once more, Weizmann offered his services to the British Government and was appointed Scientific Advisor to the Ministry of Supply. A laboratory was put at his disposal at 25 Grosvenor Crescent Mews (London, S.W.1), and there soon began a number of investigations that appeared to be of importance to the war effort, amongst them the study of the formation of aromatic hydrocarbons by high-temperature cracking, the synthesis of isoprene from 3-methylbutyn-3-ol (the product of the condensation between acetone and acetylene), and various aspects of the acetone–butyl alcohol fermentation and of the utilisation of its products. The results of the work on aromatising cracking were verified in a pilot-plant erected by the Ministry of Supply and Messrs. Manchester Oil Refinery Ltd. at the plant of that firm in Trafford Park, Manchester, and were found to warrant the establishment of a large-scale factory, albeit after the end of the war. The results of Weizmann's other investigations became of considerable importance for the solution of the problem of synthetic rubber production, so that, in 1942, Weizmann was asked to visit America and to advise the Government of the United States on that problem. Mr. Henry Wallace, then Vice-President of the United States, later gave public acknowledgment to the services which Weizmann rendered the United States in the planning of the synthetic rubber programme.

Again, the end of the war with all its political implications brought Weizmann's scientific work to a standstill—this time for good. His health, particularly his eyesight, failed, and his work at the Sieff Institute was confined to advising and supervising the younger scientists who had gradually assembled there and later at the Weizmann Institute of Science. Every achievement of the Institute, however small, was for Weizmann a source of happiness and pride, and for some years the visit to the laboratory was part of his daily routine at Rehovoth, in spite of his political work and, later, his duties as President of the State. In 1951, his illness forced him to reduce his activities to a minimum, and gradually to give them up almost completely. He bore his illness with patience and the great dignity that was so characteristic of him.

Weizmann was a man of brilliantly clear mind and at the same time of deep, warmhearted gentleness, exacting towards his co-workers as towards himself, and at the same time generous, a son of the Jewish people and a citizen of the world, a statesman and a scientist. Nobody who knew him, nobody who met him, however, will ever have felt any duality in him—there was in him a oneness of character and purpose, a deep inner peace which made him the great man he was.

## Scientific work

*Investigations in the Polycyclic Series and on Related Subjects.*—The starting point of Weizmann's studies was the fact that, in contradistinction to aromatic hydrocarbons or aryl ethers, phenols give with phthalic anhydride under the influence of catalysts, such as zinc chloride, fluoran derivatives, *e.g.*, (I) with α-naphthol. He observed that boric acid yielded the normal keto-acid, 2-*o*-carboxybenzoyl-1-naphthol (II), which could be cyclised to 11-hydroxynaphthacene-5 : 12-quinone (III). This new route to the naphthacene series was systematically explored by Weizmann and his collaborators, although their hope of obtaining new vat dyes did not materialise—we know to-day that naphthacenequinones fail to give quinols in the same way as, *e.g.*, anthraquinones (Fieser, *J. Amer. Chem. Soc.*, 1931, **53**, 2329). In this search for new dyes, Weizmann synthesised a series of more highly hydroxylated naphthacenequinones. Thus, condensation of hemipinic anhydride with 1 : 4-dihydroxynaphthalene afforded the keto-acid (IV) and eventually, after demethylation, a dye (V), an alizarin of the naphthacene series.

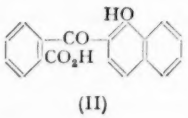
In respect to the mechanism of the boric acid synthesis, Weizmann supposed originally that a boric ester of α-naphthol is formed, which condenses more easily with phthalic anhydride than the free phenol; later, it became evident that boric acid stabilises the keto-acid (II) in form of a complex borate, *e.g.*, (VI), and thus prevents the isomerisation to (VII) which undoubtedly represents the intermediate in the formation of the undesirable naphthafluoran (I).

The condensation reactions of phthalic anhydrides that can be achieved by means of aluminium chloride or the combination of boric and sulphuric acids suffer from one disadvantage: the point of attachment of the *o*-carboxybenzoyl radical is not always unambiguous. In an attempt to find a synthetic method that would avoid this difficulty, Weizmann turned to the aromatic Grignard compounds. As early as 1905, he observed that α- and β-naphthylmagnesium bromide react with phthalic anhydride to give keto-acids (VIII and IX) which could be cyclised to 1 : 2-benzanthraquinone and naphthacenequinone, respectively. In later years, this method has been studied extensively; it has proved especially useful in the synthesis of carcinogenic hydrocarbons, in which the ability of the esters of such keto-acids to react with Grignard

compounds RMgX preferentially at the keto-group led to compounds of type (X) (see, *e.g.*, Fieser and his co-workers, *J. Amer. Chem. Soc.*, 1937, **59**, 2331; 1938, **60**, 170).

*The Aromatising Cracking of Hydrocarbons.*—The occupation with polycyclic hydrocarbons led Weizmann to a study of the mechanism by which these compounds are formed at high temperatures from various hydrocarbon materials. This investigation resulted in a technical process for the production of the whole range of aromatic hydrocarbons (and of gaseous hydro-

(I)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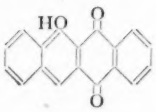
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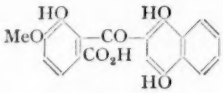
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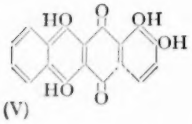
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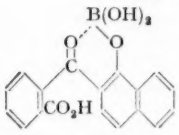
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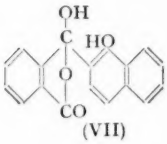
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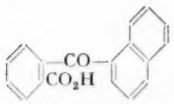
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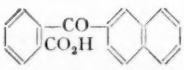
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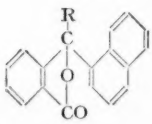
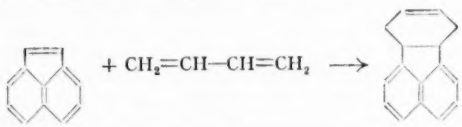

(X)

carbons, mostly of unsaturated nature) by cracking of petroleum or petroleum fractions at high temperature (680—700°) and at atmospheric pressure. The process is based on the fact that all non-aromatic hydrocarbons, independently of their structure and size, are degraded under these conditions to very small fragments, especially dienes and ethylenes, and that the latter combine by diene synthesis to hydroaromatic compounds which are eventually dehydrogenated. The investigation of this mechanism has uncovered a number of interesting new diene reactions, *e.g.*, with acenaphthylene, leading to fluoranthene derivatives:



*The Acetone–Butanol Fermentation and Related Subjects.*—Weizmann's name in the scientific world has been closely connected with the discovery of the fermentation process producing acetone and butyl alcohol from sugar and starchy materials; the bacterium which causes this fermentation (*Clostridium acetobutylicum*) was distinguished from other micro-organisms which give the same or analogous products in that it contains a starch-splitting enzyme (in addition to a powerful protease). The history of this industrially valuable discovery, and its importance for the production of smokeless powder in the First World War and of butyl acetate for the manufacture of the lacquers that the rapidly growing automobile industry in the Twenties required, are too well known to warrant repetition. However, it may be interesting to record that Weizmann intended, when he began this investigation, to find a bacterium which would produce *iso*amyl alcohol and thus provide a suitable starting material for the production of isoprene and of synthetic rubber; in the early years of this century, the price of natural rubber rose so much that a synthetic polyisoprene appeared to be able to compete with the natural material.

The chemical potentialities of the two fermentation products have been exhaustively studied by Weizmann and his associates. A special study was devoted to the Guerbet reaction of butyl alcohol, which affords, on treatment of the compound with sodium or calcium at about 280°

(under pressure), 2-ethylhexanol and butyric (and some 2-ethylhexanoic) acid; it could be shown that this reaction can be formulated as follows:

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$$

$$2CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CEt{\cdot}CHO$$

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CEt{\cdot}CHO + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHEt{\cdot}CH_2{\cdot}OH + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

The hydrogen required in the last step for the reduction of 2-ethylhex-2-enal can alternatively be supplied by 2-ethylhexanol already formed; thus, the formation of some 2-ethylhexanoic in addition to butyric acid finds its explanation. The correctness of this mechanism has been substantiated by a number of syntheses which suggested themselves on its basis, *e.g.*, the preparation of 2-alkyl*cyclo*hexanols from primary alcohols and *cyclo*hexanol.

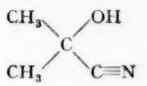
Only in later years did Weizmann turn his attention to the biochemical mechanism of the acetone–butyl alcohol fermentation. It was found that the bacterium responsible for the fermentation requires three external growth factors: biotin, asparagine, and a third compound which was later identified as *p*-aminobenzoic acid. The last acid can be replaced by a number of analogues, amongst them *p*-aminophenylalanine. A study of the enzyme systems present in the micro-organism showed that it is able to reduce fatty acids to the corresponding alcohols. One is thus led to assume that it is distinguished from the analogous bacteria which are producing fatty acids, particularly butyric acid, by the presence of this powerful reducing mechanism.

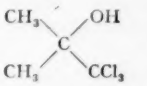
Weizmann was always conscious of the fact that this fermentation process leads to compounds containing three and four carbon atoms (in addition to some ethyl alcohol) and thus, potentially, to the substances on which the modern petrochemical processes are based. On many occasions, he stressed the technical and political implications of a change-over from a petroleum-based to a fermentation-based chemical industry, especially for countries poor in natural oil. When during the Second World War the shortage of natural rubber threatened the war effort of the Allies, and even the American petroleum industry seemed incapable of coping with the task of supplying the—identical—raw material for both synthetic rubber and aviation fuel, Weizmann suggested enlisting the help of the fermentation industry, and indeed a great part of the butadiene and the styrene used in the manufacture of synthetic rubber during the Second World War was derived from ethyl alcohol produced by fermentation processes.

*Various Subjects.*—Amongst a number of investigations in the field of amino-acids, the study of the photochemical behaviour of the aqueous solutions of these acids may be mentioned. It was found that they are hydrolysed, on irradiation, to give ammonia and the corresponding α-hydroxy-acids. This reaction was suggested as a possible pathway for the formation of the α-hydroxy-acids in green plants, which are unusually rich in a variety of these compounds. In general, Weizmann paid much attention to photochemical reactions; thus, the light-induced interaction of ketones and alcohols was studied, and the results were interpreted by a mechanism according to which an activated ketone molecule abstracts a carbon-bound hydrogen atom from the alcohol group, yielding two radicals $RR'C(OH)^{\cdot}$ which can stabilise themselves by association or disproportionation.

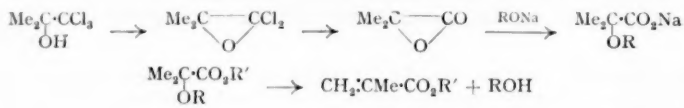
As already reported briefly, during the Second World War Weizmann and his collaborators studied many processes of potential usefulness which are mostly described in patents. Thus, the well-known reactions of ketones and acetylene to give tertiary acetylenic alcohols and glycols, $HO{\cdot}CRR'{\cdot}C{:}CH$ and $HO{\cdot}CRR'{\cdot}C{:}C{\cdot}CRR'{\cdot}OH$, could be simplified considerably. By following up some indications in the literature, it was found that the condensation can be brought about by means of potassium hydroxide in certain solvents, *e.g.*, acetals or ketals; the preparation of metal derivatives of acetylene by the use of Grignard compounds or sodium in liquid ammonia is thus avoided. The acetylene derivatives so obtained open routes to several classes of compounds of theoretical and practical interest.

The same condensing agent—potassium hydroxide in acetals—can be employed usefully for many other reactions, *e.g.*, the condensation of chloroform with aldehydes and ketones, leading to trichlorinated alcohols, such as (XII) (from acetone). These alcohols not only resemble formally the α-hydroxy-nitriles (XI) from which unsaturated acids of the methacrylic acid type are made:

(XI) 

 (XII)

they, can indeed, be converted into these important unsaturated acids, although by a somewhat indirect route. When treated with a solution of alkali in an alcohol, (XII) is transformed into the alkali salt of an α-alkoxy*iso*butyric acid; the esters of the latter can be converted, catalytically or when heated with phosphoric oxide, into the corresponding esters of methacrylic acid. The following mechanism has been suggested for this sequence of reactions:



E. D. BERGMANN.

## PRESIDENTIAL ADDRESS.

DELIVERED AT THE 112TH ANNIVERSARY MEETING OF THE CHEMICAL SOCIETY AT BURLINGTON HOUSE ON MARCH 27TH, 1953.

# *Old and New Ideas on Saturated Rearrangements.*

By C. K. INGOLD, D.Sc., F.R.I.C., F.R.S.

REARRANGEMENTS in saturated systems occur in reactions of various stoicheiometries, for example, in substitutions, eliminations, and additions. Isomeric change can be regarded as a special case of substitution with rearrangement. Despite the stoicheiometric differences, the rearrangements exhibit a close family resemblance. Their oldest history belongs to carbonyl-forming eliminations.

In 1859 Fittig discovered pinacol, and in 1860 he observed its conversion by sulphuric acid into a ketone, pinacolone (pinacolin) (*Annalen*, 1859, **110**, 17; 1860, **114**, 54). The striking feature of this change is the shifting of a methyl group from the carbon atom which is increasing its binding with oxygen, to the carbon atom which is losing its oxygen:

$$HO{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH \longrightarrow Me{\cdot}CO{\cdot}CMe_3$$

Many conversions of this type have since been realised. The original glycol need not be di-tertiary, but may at least be tertiary-secondary, tertiary-primary, or disecondary. And the shifting group need not be methyl, but may be any alkyl or aryl group.

Much work has been done on this reaction in order to determine what are called the relative migratory aptitudes of groups, though this phrase tends to mix up two questions which should be taken in order. The first is that of which hydroxyl will be lost, when the glycol $HO{\cdot}CR^1R^2{\cdot}CR^3R^4{\cdot}OH$ is treated with acid; because that determines which of the two pairs of R's will furnish an R to replace it. This being settled, the second question has meaning, namely, which member of the relevant pair of R's will be so furnished. The answers have been known since 1929 (*Ann. Reports*, 1928, **25**, 133; cf. Shoppee, Thesis, London, 1929). The first is that acid-catalysed hydroxyl loss, with rearrangement, from $RR'\dot{C}{\cdot}OH$, is facilitated by inductive and conjugative electron release from RR', just as in ordinary unimolecular substitution or elimination, without rearrangement, from the conjugate acid of an alcohol:

$$R^1R^2C\overset{\curvearrowright}{-}OH_2^+ \longrightarrow R^1R^2C^+ + OH_2$$

The second answer is that, of a given pair of groups $R^3R^4$, that group will migrate best which can best provide electrons: in other words the migrating group behaves as an internal nucleophilic reagent towards an electron-demanding centre.

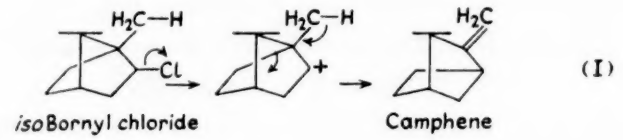
A number of rearrangements are known which are such obvious variants of the pinacol–pinacolone conversion that we can regard them as covered by our discussion of this change. They include the rearrangements of epoxides, the acyloin rearrangement, the aldehyde–ketone rearrangement, the benzil–benzilic acid conversion, the iodohydrin rearrangement, and pinacolic deamination. We shall not find it necessary to discuss them independently.

The other large group of rearrangements in saturated carbon systems belong to olefin-forming eliminations, and their reversal in the corresponding additions, and to the often concomitant nucleophilic substitutions: we call all these changes, independently of their stoicheiometry, Wagner–Meerwein rearrangements.

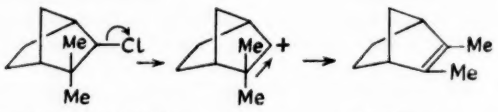
They were discovered by Wagner in 1899, who recognised them as necessary for an interpretation of relations between different dicyclic terpenes (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 680; *Ber.*, 1899, **32**, 2302). Considering that in 1899 not a single dicyclic terpene had a firmly established structure, Wagner's combined deduction of the structures and of their interrelation through a previously undiscovered type of rearrangement must be counted a work of genius. Meerwein generalised Wagner's process, carried it outside the closed circle of bridged rings, and made it a phenomenon of organic chemistry, not only one of terpene chemistry (*Annalen*, 1910, **376**, 152; 1913, **396**, 200; 1914, **405**, 129; 1918, **417**, 255). Meerwein also made a major contribution, indeed the basic one, to the elucidation of the mechanism of the change, as we shall note later.

The following formulæ illustrate some cases, taken from the field of terpene chemistry. Stoicheiometrically, some are olefin-forming eliminations (I and II), some nucleophilic sub-

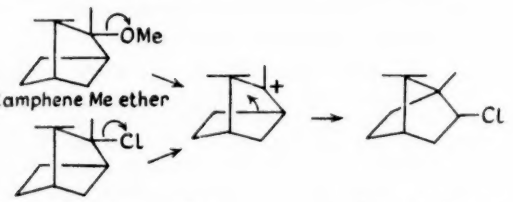
stitutions (III, and the isomeric changes, or " symmetrical substitutions," IV and V), and some olefin additions (VI and VII). In spite of that, they all conform to a common pattern, if, following Meerwein's lead, we represent them as proceeding through a carbonium ion. Either a




*iso*Bornyl chloride Camphene (I)

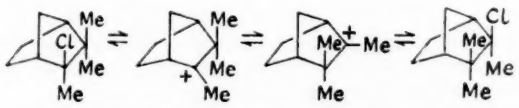



Camphenilyl chloride Santene (II)

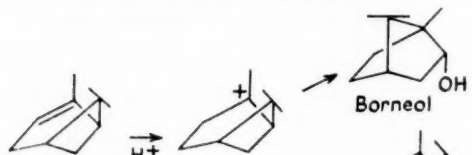



Camphene hydrochloride *iso*Bornyl chloride (III)

Pinene hydrochloride Bornyl chloride (IV)




Racemisation of camphene hydrochloride (V)




α-Pinene Borneol (VI)

Fenchyl alcohol (VII)

ring-loop or a methyl substituent may move over from adjacent tertiary or quaternary carbon to the carbonium ionic centre.

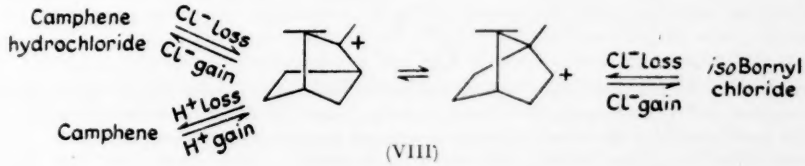
However, there are evident stereochemical restrictions on what does move over. For we cannot but notice that, in olefin-forming eliminations (I) and substitutions (III and IV), the initially detached substituent leaves carbon from the side opposite that to which the ring-loop becomes bound; and likewise that, in substitutions (III and IV) and olefin additions (VI and VII), the finally entering substituent becomes bound to carbon on the side opposite that from which the ring-loop leaves.

When a methyl group shifts, as in santene formation (II), or in the interpretation (Simonsen and Owen, " The Terpenes," Vol. II, Cambridge Univ. Press, 1949, p. 290) of the racemisation of camphene hydrochloride (VI), and hence of camphene or of *iso*bornyl chloride, the stereochemical rules may well be the same, though this cannot be deduced from the structures concerned in the absence of isotopic labelling.

As before, we shall not separately consider obvious variants of the main process, but will take the Demjanow rearrangement, for example, to be included by implication in our discussion of Wagner–Meerwein changes.

The early theories of pinacol–pinacolone and related rearrangements need not long engage our attention. About 1880, Breuer and Zincke suggested epoxides (*Annalen*, 1879, **198**, 141), and Erlenmeyer *cyclo*propanes (*Ber.*, 1881, **14**, 322), as intermediates. But at that time little was known of the properties of either epoxides or *cyclo*propenes. In 1905, Tiffeneau advanced the hypothesis of free-radical intermediates (*Bull. Soc. chim.*, 1907, **1**, 1221). Again, at that date no one knew much about free radicals. As our knowledge grew of the types of structures postulated, all these theories were seen to be inadequate.

The year 1922 marks, with a paper by Meerwein and van Emster, the beginning of the modern theory of saturated rearrangements (*Ber.*, 1922, **55**, 2500). These authors had made a kinetic study of certain rearrangements, notably, the conversion of camphene hydrochloride into *iso*bornyl chloride; and they built up a strong case for the view that these rearrangements depend on ionisation, the alteration of carbon framework occurring in the carbonium-ion stage (VIII):




(VIII)

They offered two main reasons for this view. One was that the first-order conversion rates depended on solvent in a way which was clearly to do with ionising power, as could be checked by reference to the ionisation of triphenylmethyl chloride in the same solvents. The other reason was that those inorganic halides, such as $SnCl_4$, $SbCl_3$, and several others, which form additive ionic compounds with triphenylmethyl chloride, are powerful catalysts for rearrangement, while those, such as $SiCl_4$, $PCl_3$, which do not unite with triphenylmethyl chloride, do not catalyse rearrangement. Later, Meerwein with other collaborators added a third reason, namely, that mobility increases with the stability of the detachable substituent, as an anion: among camphene esters, for example, the following rate series was established (*Annalen*, 1927, **453**, 16):

arylsulphonate > bromide > chloride > trichloroacetate > nitrobenzoate

Later still, in 1929, I supplied a fourth reason, which was the point mentioned already, namely, that electron-supply to the atom from which, according to theory, the anion is required to separate, is indeed needed to facilitate the rearrangement. And so, by 1930, a very substantial body of evidence had been accumulated in favour of Meerwein's theory.

During the 1930's Whitmore extended our knowledge of the Wagner–Meerwein change in the acyclic series (*J. Amer. Chem. Soc.*, 1932, **54**, 3431; 1933, **55**, 4161; 1939, **61**, 1586). He found that *neo*pentyl alcohol and its halides would undergo certain standard forms of nucleophilic substitution only with great reluctance; but that such substitutions, with accompanying eliminations, could easily be effected by certain special methods, for instance, by treatment of the halides with aqueous silver or mercuric salts; and that then the products are rearranged *tert.*-amyl compounds or *iso*amylene. In 1946 Dostrovsky and Hughes carried this demonstration to a conclusion [*J.*, 1946, 157 *et seq.* (6 papers)]. They showed kinetically that the substitutions that proceeded tardily were $S_N2$ substitutions, and that the products were unrearranged, as in the following example:

$$CMe_3{\cdot}CH_2{\cdot}Br \xrightarrow[S_N2]{OEt^- \text{ in EtOH}} CMe_3{\cdot}CH_2{\cdot}OEt$$

They showed also that the ready nucleophilic substitutions or eliminations were unimolecular

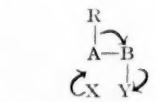
processes $S_N1$, or catalysed unimolecular processes, and that when this type of mechanism could be kinetically established, the products were rearranged, as indicated below :

$$CMe_3{\cdot}CH_2{\cdot}Br \xrightarrow[S_N1 + E1]{50\%\ \text{Aq. EtOH}} \begin{cases} HO{\cdot}CMe_2{\cdot}CH_2Me \\ EtO{\cdot}CMe_2{\cdot}CH_2Me \\ CMe_2{:}CHMe \end{cases}$$

This kinetic work at once linked up the study of rearrangements with that of unimolecular reactions of substitution and elimination in general, and thus brought to bear on the rearrangement problem the whole weight of our accumulated knowledge of the mechanism of unimolecular reactions. The subsequent study of saturated rearrangements derives its direction from this link-up.

First, however, there is a little more to be said about the work of the 1930's, and early 1940's. Notably, Whitmore pointed out that rearrangements are known, which are similar to the pinacol–pinacone and Wagner–Meerwein rearrangements, but involve nitrogen-containing systems, as in the Curtius, Hofmann, and Lossen rearrangements (*J. Amer. Chem. Soc.*, 1932, **54**, 3274). All these reactions can be regarded as dependent on the production of an electron-deficient atom, whether carbon or nitrogen.

Then, as to the stereochemistry of saturated rearrangements, a number of early results were available to convince us, as illustrated already, that we have configurational inversion at atom A from which migration starts, and also inversion at atom B on which migration ends, as indicated in the following expression :




This is written as for a substitution, but by the prior insertion of a bond AX, it can do duty for an elimination, and by making the B–Y bond initially double, it can serve for the case of addition. The older results, such as have been illustrated, applied primarily to Wagner–Meerwein changes; but it was shown in the later 1930's, particularly by Bartlett (*J. Amer. Chem. Soc.*, 1937, **59**, 820; 1938, **60**, 2416; 1940, **62**, 2927) and by Whitmore (*ibid.*, 1939, **61**, 1324), that similar conclusions hold for pinacol–pinacone rearrangements.

As to the configurational effect in the migrating group R, it has not even yet been directly proved for the pinacol–pinacone or Wagner–Meerwein changes, but it has been shown, particularly by Wallis (*J. Amer. Chem. Soc.*, 1926, **48**, 169; 1931, **53**, 2787; 1933, **55**, 1701; 1941, **63**, 1674) and by Kenyon (*J.*, 1939, 916; 1941, 263; 1946, 25), for the related Beckmann, Curtius, Hofmann, Lossen, Schmidt, and Wolff rearrangements, that at this point in the molecule configuration is preserved.

Since 1946 the objective of investigation has shifted from the space-relations to the time-relations between the component covalency changes. It is convenient for some purposes to regard the rearrangement as two substitutions, one at B and one at A, interconnected by the migration of R. We have to ask, first, whether the electron transfers at B are synchronous or not, that is, $S_N2$-like or $S_N1$-like, and, secondly, whether those at A are synchronous or not. We shall find that either question may have either answer, and that, consequently, a plurality of mechanism, similar to that encountered in more elementary reactions, applies also to these rearrangements.

We should note that the spatial relations between the covalency changes do not answer these questions, except in a permissive way. If substitution at B, for instance, were $S_N2$-like, then there would be inversion. But so there would if it were $S_N1$-like, provided that R begins to move over before Y has receded out of shielding range, say, about 5 Å. The stereochemical result shows only that R does begin to move over before Y has gone as far as that.

However, the energetically important question is whether R begins to move over before Y has receded to its transition-state distance, that is, by about 0·35 Å. If it does not, then the separation of Y will not be kinetically affected by the migration of R, and the substitution at B will be classed as step-wise, or $S_N1$-like. Its rate will be about the same as that of any unimolecular reaction in which the same type of heterolysing bond has the same immediate local surroundings in simple molecules. If the migration of R does begin before Y has receded to its transition-state distance, then the substitution will be $S_N2$-like. The reaction will now be " accelerated "; this means that we may find it going thousands of times faster than if the same heterolysing bond had the same local surroundings in simple non-rearranging molecules.

Our rate standards are quite definite to within structurally trivial factors, such as 2 or 3. In

unimolecular reactions we have no general complications due to steric hindrance, and therefore, in saturated systems, in which weak polar effects are largely localised, rate of heterolysis structurally depends essentially on the heterolysing bond and the atoms immediately next to it. Thus to within the limits mentioned, all tertiary alkyl chlorides are heterolysed at the same rate, as is illustrated by the following relative rates of solvolysis in 80% aqueous alcohol at 35°; and all tertiary iodides are also heterolysed at almost the same rate:

| | $Me{\cdot}CMe_2{\cdot}$ | $Et{\cdot}CMe_2{\cdot}$ | $Pr^n{\cdot}CMe_2{\cdot}$ | $Bu^n{\cdot}CMe_2{\cdot}$ | $n\text{-}C_5H_{11}{\cdot}CMe_2{\cdot}$ |
|---|---|---|---|---|---|
| Chlorides ..... | 1·00 | 1·61 | 1·41 | 1·33 | 1·21 |
| Iodides ..... | 1·00 | 1·85 | 1·77 | 1·75 | 1·53 |

So are tertiary alkylsulphonium salts, and likewise secondary alkyl bromides, primary alkyl bromides, and so on—always, be it noted, as long as the reactions remain unimolecular.

Against that background, let us notice some rates of rearranging reactions. Most of the examples I shall give are due to Prof. E. D. Hughes and his colleagues and pupils, who have been studying this subject since they published their linking-up papers of 1946. The simplest case is the solvolysis of *neo*pentyl bromide to give *tert.*-amyl products (Dostrovsky and Hughes, *J.*, 1946, **164**, 166, 171). As the following figures illustrate, the unimolecular rate is about the same as for other primary bromides, for instance, ethyl bromide:

Hydrolysis in wet $H{\cdot}CO_2H$ at 95° { ethyl bromide, $k_1 = 2{\cdot}70 \times 10^{-6}$ sec.$^{-1}$; *neo*pentyl bromide, $k_1 = 1{\cdot}53 \times 10^{-6}$ sec.$^{-1}$

Evidently the migrating methyl group in the *neo*pentyl group does not assist heterolysis of the halogen, even though the migration must occur before the halogen has passed out of shielding range, since no appreciable quantities of unrearranged solvolysis products accompany the rearranged products. Again, as the next set of figures exemplifies (Hughes *et al.*, *Nature*, 1950, **166**, 679) the solvolysis of pinacolyl chloride, $CMe_3{\cdot}CHMe{\cdot}Cl$, also to give exclusively rearranged products, goes at almost the same unimolecular rate as would apply to any simple secondary chloride, such as *iso*propyl chloride:

Solvolysis in 80% aq. EtOH at 80° { *iso*propyl chloride, $k_1 \sim 5 \times 10^{-7}$ sec.$^{-1}$; pinacolyl chloride, $k_1 = 1{\cdot}94 \times 10^{-7}$ sec.$^{-1}$

Now let us notice some accelerated rearrangements. Hughes obtained one by replacing the three methyl groups of *neo*pentyl chloride by three phenyl groups, to give **2 : 2 : 2**-triphenylethyl chloride, which is solvolysed with exclusive rearrangement to give triphenylethylene:

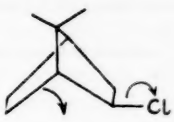
$$CPh_3{\cdot}CH_2{\cdot}Cl \longrightarrow CPh_2{:}CHPh$$

But this solvolysis in formic acid goes 60,000 times faster than that of *neo*pentyl chloride, and therefore faster by factors of that order than those of simple non-rearranging primary chlorides (Charlton, Dostrovsky, and Hughes, *Nature*, 1951, **167**, 986):

Hydrolysis in wet $H{\cdot}CO_2H$ at 95° { *neo*pentyl chloride, $k_1 \sim 4 \times 10^{-6}$ sec.$^{-1}$; **2 : 2 : 2**-triphenylethyl chloride, $k_1 = 2{\cdot}3 \times 10^{-3}$ sec.$^{-1}$

Here, the migrating phenyl group is evidently helping to detach the chlorine, thus acting in a synchronous, $S_N2$-like manner. The resulting acceleration has been called a *synartetic* acceleration, for a reason which will be explained later.

Bornyl and *iso*bornyl chloride provide an interesting comparison among secondary alkyl chlorides. The solvolysis of bornyl chloride is unaccelerated. Its rate is compared below with that for pinacolyl chloride, which we have already compared with the rate for *iso*propyl




*iso*Bornyl chloride
**(IX)**

Bornyl chloride
**(X)**

chloride. The solvolysis rate of *iso*bornyl chloride is about 100,000 times greater (Brown, Hughes, Ingold, and Smith, *Nature*, 1951, **168**, 65):

Solvolysis in 80% aq. EtOH at 80° { pinacolyl chloride, $k_1 = 1{\cdot}94 \times 10^{-7}$ sec.$^{-1}$; bornyl chloride, $k_1 = 1{\cdot}5 \times 10^{-7}$ sec.$^{-1}$; *iso*bornyl chloride, $k_1 = 1{\cdot}4 \times 10^{-2}$ sec.$^{-1}$

The products from either isomer are camphene derivatives. The idea that the fast reaction owes its high rate to synartetic acceleration accords well with the stereochemical situation. For in the *iso*bornyl compound the bond shift could be initiated before the chlorine had receded to the separation of the transition state of its ionisation, and therefore could have an accelerative effect on the rate (IX). But in bornyl chloride, no bond shift can commence until the chlorine has moved right out of the way, to well beyond the transition-state separation, and therefore the bond shift must come in too late to influence the rate (X).

In these examples we have the dual answer concerning the relative timing of covalency changes at atom B, on which migration ends. A similar duality could be illustrated for atom A, from which migration begins; but we can assume that to follow, without special illustration, from the known reversibility of Wagner–Meerwein rearrangements, A and B having interchangeable functions. When we put the two dualities together, we obtain at first, as the following Table shows, a four-fold classification, according to whether the three covalency changes are all separate in time, or whether the first two, or the second two, or all three, become synchronised. But, actually the fourth class cannot be illustrated; and the second and third are only forward and backward readings of the same reversible reaction. Thus we have two established kinetic types of rearrangement, which we may call the " normal-rate " type and the " accelerated " type.

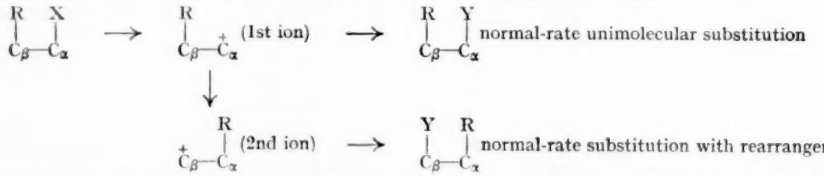
| | Molecularity of " substitutions " at | | Timing of the electron transfers (*c* R *b* *a*; Y A B X) | Example | Kinetic type |
|---|---|---|---|---|---|
| | B | A | | | |
| (1) | uni | uni | *a*, then *b*, then *c* | *neo*Pentyl ⟶ *tert.*-amyl | Normal |
| (2) | bi | uni | *a* + *b*, then *c* | *iso*Bornyl ⟶ camphene | Accel. |
| (3) | uni | bi | *a*, then *b* + *c* | Camphene ⟶ *iso*bornyl | Accel. |
| (4) | bi | bi | *a* + *b* + *c* | (None established) | — |

As I have remarked already, the whole of this contemporary investigation of rearrangements arises from its absorption into the study of unimolecular reactions; and we have, indeed, been taking as our rate standards the rates of non-rearranging unimolecular reactions. Therefore the result next to be mentioned seems, at first sight, very surprising. It is that even non-rearranging unimolecular reactions are known which are accelerated. This may happen when the structure is prone to rearrangement, even if the rearrangement does not actually occur in the reaction showing the rate increase. The most familiar example is the aqueous hydrolysis of camphene hydrochloride to camphene hydrate and camphene. There is no rearrangement; but the rate is too great to be measured, and is obviously much greater than for simple tertiary chlorides. The rate of the corresponding ethyl alcoholysis has been measured by Hughes and his colleagues, and has been found to be 6000 times greater than for *tert.*-butyl chloride (*idem, ibid.*):

Solvolysis in dry EtOH at 0°: { *tert.*-butyl chloride, $k_1 \sim 7 \times 10^{-9}$ sec.$^{-1}$ ; camphene hydrochoride, $k_1 = 4{\cdot}0 \times 10^{-5}$ sec.$^{-1}$ }

We interpret this as a quantal phenomenon, somewhat analogous to optical refraction or polarisability, which for any molecular state depends on all the *other* states the molecule *could* get into, even though the molecule is not utilising those possibilities.

As a preliminary to a more careful consideration (*idem, ibid.*) of this, and of the other phenomena illustrated above, let us start by restating Meerwein's theory in its wider setting of unimolecular reactions, as is here done in terms of chemical formulæ:




The rate-controlling step is heterolysis of the bond $C_\alpha$—X to give a carbonium ion. As the possibility of rearrangement has to be taken into account, we may call the obvious structure of this ion that of the " 1st " carbonium ion. If this takes up an anion, or loses a proton, we have a non-rearranging unimolecular reaction. As we shall show, it is a normal-rate non-rearranging reaction. However, it is possible that a carbon atom with its full octet of electrons may move over from an adjoining position to the charge centre of the " 1st " ion, thus producing a " 2nd "

carbonium ion. If this takes up an anion, or loses a proton, we have rearrangement. We shall show that this is a normal-rate rearrangement.

The same theory is expressed in curves in Fig. 1, provided that we fix attention on the broken line there shown. Energy is being plotted against a reaction co-ordinate. The first diagram might represent *tert.*-amyl bromide ionising to give the *tert.*-amyl cation, which then simply yields *tert.*-amyl products. The representative point enters the diagram from the left, and goes out the same way, because the left-hand barrier lies lower. The possible rearrangement does not occur, because the energy barrier for ionisation of the *neo*pentyl system, shown on the right of the diagram, stands higher. The theoretical possibility of such a rearrangement does not affect the left-hand energy levels, that of the 1st ion, and that of the transition state of its formation; and so we observe a normal-rate unimolecular reaction without rearrangement. The broken-line curve in the second diagram might represent *neo*pentyl bromide ionising to the *neo*pentyl cation, which then goes into the *tert.*-amyl cation, and finally into *tert.*-amyl products. Here, the representative point passes through from left to right. However, the later steps do not affect the energy of the " 1st " ion, nor that of the transition state of its formation; and thus the total reaction is a normal-rate process, although it involves rearrangement.

FIG. 1.

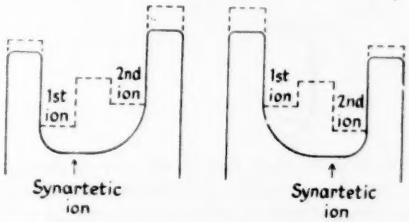



FIG. 2.

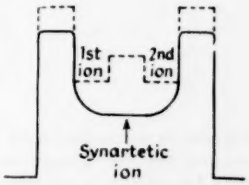
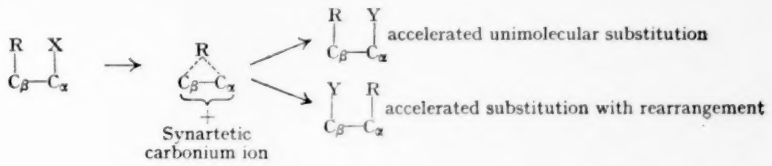



FIG. 1. *Schematic representation of non-rearranging (left) and rearranging (right) unimolecular reactions, without (broken lines) and with (full lines) synartetic acceleration. Energy is being plotted against a reaction co-ordinate. The representative points enter from the left and leave mainly over whichever lateral energy-barrier lies lower.*

FIG. 2. *Schematic representation of symmetrical unimolecular substitutions, without (broken line) and with (full line) synartetic acceleration. Energy is plotted against a reaction co-ordinate. The representative points enter from the left, and leave equally by the left and by the right, so that there is 50% of rearrangement.*

Now suppose that the barrier between 1st and 2nd ions is removed. The two ions will then cease to exist as individuals, their formulæ becoming no more than representations of brackets to the extra uncertainty of position now attaching to certain electrons. In our usual inaccurate language, we shall say that their resonance has produced a single ion more stable than either, a *synartetic ion*, as we may call it. The name means " to fasten together," because a single bond, that of the migratory group, is coupling the locations of an ionic charge split between the two possible centres. We have a more stable ion. Therefore we have more stable transition states of its formation, as shown by the full-line curves of Fig. 1. This follows because transition states, which themselves can be treated as resonance structures, reflect the stability changes of their factors and products. These full-line curves, then, having lowered energy barriers, illustrate accelerated reactions. The left-hand diagram might now represent the hydrolysis of camphene hydrochloride to camphene hydrate: it is accelerated, but goes without rearrangement. However, the acceleration is connected in an essential way with the presence of the molecular mechanism for accelerated rearrangement. The full-line curve in the right-hand diagram might represent the conversion of *iso*bornyl chloride into camphene: it is accelerated, and goes with rearrangement.

We may now back-translate this extension of the Meerwein theory into terms of chemical formulæ:

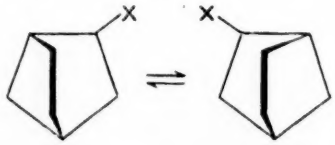


The rate-controlling stage is still the heterolysis of the bond $C_\alpha$—X; but now the more stable synartetic ion is produced, and thus all unimolecular reactions are accelerated; whilst, according to the position in which the synartetic ion is attacked, the reactions will go without or with rearrangement. It will be clear why, no matter whether rearrangement occurs or not, we classify the accelerations as synartetic.

The symmetrical case, represented in Fig. 2, is realised when factor and rearrangement product are mirror-images, so that rearrangement can be followed by loss of optical activity. Cram has discovered a normal-rate case of this in the 1-methyl-2-phenylpropyl-toluenesulphonates (*J. Amer. Chem. Soc.*, 1949, **71**, 3863) :

$$\begin{matrix} \text{CHMe·CHMe} \\ | \quad\quad | \\ \text{Ph} \quad \text{OTs} \end{matrix} \rightleftharpoons \begin{matrix} \text{CHMe·CHMe} \\ | \quad\quad | \\ \text{OTs} \quad \text{Ph} \end{matrix} \qquad (\text{Ts} = p\text{-}C_6H_4Me\cdot SO_2)$$

Winstein and his collaborators have found a case involving a mild degree of acceleration in the *exo*-norbornyl benzenesulphonates whose rearrangement is like an *iso*bornyl-ester–camphene–ester conversion, but with the three methyl groups removed, so that rearranged isomers become enantiomers (*ibid.*, 1952, **74**, 1127) :




Synartesis is concerned with the distribution over more than two atoms of σ-electrons only, and does not involve π-electrons. Mesomerism, on the contrary, is basically concerned with more-than-two-centre π-electrons. Furthermore, the pattern of valency and charge distribution in synartesis is quite different from that in mesomerism. Evidently the two phenomena are different enough to be treated as distinct.

The next question to which investigators will have to address themselves is obvious : When will synartetic acceleration occur, and when not? I think myself that the full answer will involve several conditions, including a suitable stereochemical arrangement and the absence of adequate stabilisation of an original cationic centre by mesomerism, that is, by ordinary conjugation or hyperconjugation. It appears, however, that, the necessary structural conditions being fulfilled, the carbonium carbon atom can do, what the isoelectronic neutral boron atom is certainly able to do, namely, split up σ-bonds. Such splitting seems always to take place when the only alternative would be to leave the fourth valency orbital unoccupied.

HERMAN WALTHER NERNST

[*To face p.* 2853.

# *The Nernst Memorial Lecture.*

## HERMANN WALTHER NERNST.

DELIVERED BEFORE THE CHEMICAL SOCIETY AT BURLINGTON HOUSE ON MARCH 19TH, 1953.

By J. R. PARTINGTON, M.B.E., D.Sc.

ABOUT twenty miles north-east of Torun (Thorn), the birthplace of Copernicus, is a small town, once in West Prussia and called Briesen, now in Poland and renamed Wabrezno. It was there, on June 25th, 1864, that Hermann Walther Nernst was born. His father, Gustav Nernst, who had married Ottilie Nerger, was posted at Briesen as a Prussian civil servant, but the Nernst family had lived for several generations in the town of Prenzlau, about fifty miles north of Berlin. One of them, early in the century, was a Lutheran pastor; another later farmed a large estate. Walther attended the Gymnasium at Graudenz, near Briesen, a large town now in Poland and renamed Grudziadz. He showed great ability in literature, poetry, and the classics, especially Latin composition, and later passed out as head boy of the school. His teacher in chemistry had aroused his interest in that science, and he made experiments in a small home laboratory. He then studied science in the Universities of Zürich, Würzburg, and Graz. In Graz he worked with Professor Albert von Ettinghausen, with whom he published in 1886—87 researches on the Ettinghausen–Nernst effect, which is a potential difference established across the sides of a metal plate down which heat is flowing in a temperature gradient, when a magnetic field is applied perpendicular to the flow of heat. This effect forms part of the experimental foundation of the modern electronic theory of metals, according to which both thermal and electrical conduction are due to the motion of electrons. Those moving from the hotter part of the metal have higher velocities and are, in consequence, more deflected in the magnetic field than the slower electrons from the cooler part of the metal. Nernst dedicated his book, "Theoretical Chemistry," to von Ettinghausen, "in treuer Erinnerung an seine Lehr- und Wanderjahre." In Graz he also met Boltzmann and Arrhenius. He took his degree of Ph.D. in 1887 at Würzburg under Friedrich Kohlrausch, famous for his work on the electrical conductivities of salt solutions.

Nernst thus started as a physicist, and in his later work his approach to physical chemistry was through physics. He rarely used organic compounds in his work, one exception being in his investigations with Hohmann (1893) on the equilibrium between amylene (pentene) and trichloroacetic acid:

$$CCl_3{\cdot}CO_2H + C_5H_{10} \rightleftharpoons CCl_3{\cdot}CO_2C_5H_{11}$$

which, they showed, obeyed the law of mass action. Nernst's transition from physics to physical chemistry was mainly due to the influence of Ostwald, whom he joined as assistant in Leipzig in 1887. Ostwald was actively developing and expounding the new physical chemistry, founded on the gaseous theory of solutions stated by van't Hoff in 1886, and the theory of electrolytic dissociation proposed by Arrhenius in 1887. These, and the study of chemical statics and dynamics, formed a rapidly extending field of investigation, which Nernst entered with enthusiasm and effect. From the first he was a warm supporter of the ionic theory, and he and Ostwald described an experiment to demonstrate the existence of free ions by their motion in an electrostatic field.

Ostwald was becoming increasingly interested in the significance of energy in physico-chemical processes, which he developed along the lines of what he called (following Rankine) "energetics," and he emphasised the importance to chemistry of both laws of thermodynamics. Nernst had a very sound knowledge of thermodynamics, derived mainly from Helmholtz. He differed from Ostwald in emphasising the importance of the atomic and molecular theories, and the title of his text-book, "Theoretical Chemistry, from the Standpoint of Avogadro's Rule and Thermodynamics" (first published in 1893), expressed his attitude towards the two main foundations of the science. This book in its several editions and translations was widely used for many years. It is not an easy book, but any student who could make a way through its thirty chapters would emerge well equipped to begin research. Although he gave a good account of the phase rule in the book, Nernst thought its importance had been exaggerated, saying that "the molecular theory, the thermodynamics of incomplete equilibria, and above all

the law of mass action, are points of view of immensely greater importance and much deeper content than the schemes of the phase rule, however useful and necessary this may sometimes be in chemical research"; and he quotes van't Hoff [1] to the same effect.

Nernst had a sound mathematical competence. In the second half of the nineteenth century, even the elements of the calculus were generally regarded by chemists as superfluous. This may be true in some branches of chemistry, but in physical chemistry the spirit and methods of mathematics are indispensable. In collaboration with Schoenflies, the mathematical crystallographer, Nernst published in 1895 a small book, "Einführung in die mathematische Behandlung der Naturwissenschaften," which reached an eleventh edition in 1931. He disliked unnecessarily complicated or lengthy mathematics, and in his text-book of theoretical chemistry many intermediate steps must be supplied by the reader. His concise style enabled him to cover a large field in the book and it shows a wide knowledge of the literature. It mentions Waterston's paper on the kinetic theory of gases, read to the Royal Society in 1845 but first published, at the instance of Lord Rayleigh, in 1892; and it summarises the memoir of Jellett, of Dublin, on the optical investigation of mass action, published in 1873, work which Nernst said was conducted with great experimental skill and led to important theoretical results. Jellett's memoir was edited by Nernst for Ostwald's *Klassiker*.

In 1890 Nernst went as assistant to Riecke, professor of physics in Göttingen, and he became assistant professor of physics in 1891. In 1892 he married Emma Lohmeyer, daughter of an eminent surgeon. Those who met Frau Nernst can testify to her sincerity and charm. He owed much to her steadfastness and devotion, and many of his students must remember with gratitude her kindness, and her understanding of the difficulties of young people transplanted into a strange environment.

Although he was invited to succeed Boltzmann in Munich, Nernst was faithful to Göttingen, where in 1894 he became the first professor of physical chemistry and was provided with an Institute, in which he soon built up an active school of research, especially in electrochemistry and chemical thermodynamics. Many of his students in Göttingen, who came from all parts, were afterwards leaders in physical chemistry. He became Geheimrat in 1904, but in that year he was called to succeed Hans Landolt as professor of physical chemistry in Berlin. In the Autumn of 1905 he took up his duties in the second Chemical Laboratory, which was renamed the Physico-Chemical Laboratory, in the Bunsenstrasse. Emil Fischer was in Berlin, and was perhaps the most outstanding and brilliant chemist of the time, yet the fame of Nernst drew to his laboratory a good share of research students, and his school maintained its place alongside that of the great master of organic chemistry.

It was in Berlin, in 1911—13, that I had the good fortune to work in Nernst's laboratory. The arrangements were rather primitive, and although the Steward, Woicke, was helpful, practically everything, even corks, had to be bought outside. Nernst came round and spoke to everybody daily, asking for details of progress, if any. He was a man rather under middle height, at that time inclined to plumpness, wearing *pince nez* and formal morning dress, looking like a banker or a high business executive, and with a quiet voice and manner.* The assistants, von Wartenberg, Eucken, von Siemens, and Koref, were highly skilled experimenters, and helpful with advice and suggestions. The students were cheerful and friendly, and there was an atmosphere of optimism and comradeship which helped to tide over the difficulties inseparable from research in physical chemistry. The Professor was a most skilful and resourceful experimenter, with a profound distrust of large, complicated, and expensive apparatus. Electrical conductivities were measured at room temperature, not in a thermostat, and temperature-coefficient corrections applied. Wire resistances were replaced by Magnanini liquid resistances. One had first to accept some old apparatus and make it work, then new apparatus was either provided or allowed to be made. Even the simplest apparatus had to perform accurately the task allotted to it. My apparatus was necessarily rather large, and when Nernst saw it set up he refused to speak to me for a day or two. When he saw that its size was unavoidable, he relented, and provided me with his own post-office box and a new string galvanometer.

The Institute in 1911 was supplied with liquid hydrogen by an apparatus of Nernst's invention, which was made and sold by the mechanic, Hoenow, for £20. Nernst was then trying, with the assistance of Dr. F. A. Lindemann (now Lord Cherwell) and his brother, C. Lindemann, to make liquid helium. One morning the precious stock of helium (obtained from pitchblende) was under compression when the apparatus burst. I saw Nernst spreading

[1] See also *Naturwiss.*, 1939, **27**, 393.

* The portrait reproduced facing p. 2853 is from a photograph taken in 1904.

the sides of his coat over the compressor in a vain attempt to catch the escaping gas, and saying pitifully : " Das Helium ! Das Helium ! "

Nernst's lectures on physical chemistry, delivered from 3 to 5 o'clock in the afternoon, with a short break at 4, mostly followed his book, and were enlivened by good experiments, personal anecdotes, and interesting criticisms. I remember his saying that, although Thomsen read his thermometers through telescopes, Berthelot obtained better results by avoiding large errors and sparing unnecessary refinements. Nernst himself, in an early research, had corrected Thomsen's values for the heats of formation of mercury compounds by using as a calorimeter a beaker with the rim cut off, standing on corks inside another beaker, and a very accurate and carefully calibrated thermometer. The results removed an apparent discrepancy with the Helmholtz equation for the electromotive force of a galvanic cell. A course of popular lectures on modern atomistics which Nernst gave in my time were well attended and much appreciated by non-specialists.

Nernst was mechanically minded. He was one of the first to run a motor car in Göttingen. On the outbreak of war in 1914 he left for active service in his small car, and accompanied the German army through Belgium to the Marne. His two sons also left for the front, and neither returned. He was awarded the Iron Cross of the first and of the second class for bravery in face of the enemy, and also the Pour le Mérite, the highest civil award. It is said that Nernst had some share in the early stages of gas warfare, but the Memorial Lecture on Haber fixes the main responsibility for this beyond doubt.

Nernst was mainly instrumental, through his personal influence with Ernest Solvay, in the foundation of the Solvay Conferences, in which he participated with considerable effect. He was also largely responsible for the creation of the Kaiser Wilhelm Institutes, which played an important part in the development of German science and industry after the first World War.

Nernst remained at the Institute in the Bunsenstrasse until 1922, when he succeeded Warburg as President of the Physikalisch-Technisches Reichsanstalt. Here he probably felt less at home than in academic surroundings, and his stay was short. Nernst was a great admirer of Shakespeare, and it is said that in a conference concerned with naming units after appropriate persons, he proposed that the unit of rate of liquid flow should be called the falstaff. He left the Reichsanstalt in 1924 to succeed Rubens as professor of physics and Director of the Physical Laboratory, which post he held until his retirement in 1933. The rest of his life was spent on his country estate, Zibelle, in Muskau, Lausitz, now on the border of Silesia and Poland. There he followed his interests in agriculture, fishing, and shooting, and there he died on November 18th, 1941. His remains were afterwards reinterred in Göttingen.

Although associated with some of the outstanding theories in physical chemistry, Nernst was highly practical and inventive, and was much interested in the applications of science in industry and daily life. In 1897 he realised that the highest temperature attainable in the carbon-filament electric lamp was too low for efficiency, and he replaced the carbon by a rod of a mixture of zirconia and rare earths. This is non-conducting at room temperature and requires preliminary heating by a spiral of platinum wire enclosed in porcelain. When the glower lights up, the heater is cut out by an automatic switch. Another difficulty now enters, *viz.*, the progressive fall in resistance of the glower with rise of temperature, which would lead to excessive current. This was corrected by having in series with the glower a spiral of fine iron wire enclosed in a bulb of hydrogen at low pressure. Iron shows an abnormal rise of resistance at a dull red-heat, and keeps the overall resistance constant. The conductivity of the glower is electrolytic, the metals which tend to be liberated being reoxidised by the surrounding air. The lamp had an efficiency of about 1½ watts per candle power, compared with 4 watts for the carbon lamp. The Nernst lamp later gave way to the metal-filament lamp, with an efficiency of ½ watt per candle power, but fortunately he was able to derive a substantial benefit from his invention, selling his patents outright to the A.E.G. for the sum of a million marks. The firm had a high opinion of Nernst's business ability as well as of his scientific eminence, and he was offered a directorship.

Nernst was a joint inventor with Dolezalek of an improved quadrant electrometer; he invented and demonstrated an electrolytic phonograph, and described some experiments which threw doubt on the value of the process of drying peat by electroendosmosis.

The Neo-Bechstein piano, invented by Nernst about 1922, depended on the electronic amplification of the sound produced by a small instrument so as to give the effect of a grand piano. The idea is very characteristic of him, but the instrument was not then a commercial success.

Nernst was fond of travel and became personally acquanted with many of the scientists of Europe and the two Americas. He gave the Silliman Lectures at Yale University in 1906, the

special University Lectures in London in 1913, and a course at La Plata. All these lectures were published. His last visit to England, to receive the honorary Doctor of Science of Oxford, was in 1937. He became an Honorary Member of the Royal Institution in 1899, Honorary Fellow of the Chemical Society in 1911, and Foreign Member of the Royal Society in 1932. He received the 1920 Nobel Prize for chemistry in 1921, and was Rector of the University of Berlin in 1921—22.

Nernst's outstanding characteristics were his directness of approach, his versatility, and his great receptivity for new ideas. Although his mind worked rapidly, he was most painstaking and patient, and would spend much time and effort in numerical calculations. His approach to theory was largely through numerical data, in which he took a great interest: he would arrange and classify them until they gave up some general law. His mental quickness could be disconcerting. In an informal lecture he might break in with questions, suggestions, and criticisms, which could put a less nimble wit out of its stride. He was never, in my experience, knowingly unkind in such cases, although he could be rather dogmatic. In taking up new theories, he liked to reshape them in his own way, leaving out the unessential parts and simplifying the rest.

I must now attempt to give some account of the main features of Nernst's scientific work. This covered many fields, but the main parts can be put under five heads: (1) electrochemistry; (2) the theory of solutions; (3) thermodynamics and chemical equilibria; (4) the solid state; (5) photochemistry. It should be realised that many publications by his students in their names alone embody some important ideas suggested by Nernst.

## Electrochemistry

The theory of electrolytic dissociation, proposed by Arrhenius in 1887, when taken in conjunction with the earlier measurements by Hittorf and Kohlrausch of the mobilites of ions, gave a convincing picture of the mechanism of electrolytic conduction, but a large and important branch of electrochemistry still awaited theoretical explanation. This concerned the electromotive forces of galvanic cells. From the time of Volta, two apparently conflicting theories had divided the allegiance of electrochemists. Volta, Davy, and Berzelius supported the contact theory, which located the seat of the electromotive force at the contact of two different metals. The chemical theory, advocated by Faraday and by Auguste de la Rive, sought the origin of the electric current in the chemical reaction in the cell. About 1850, Helmholtz and Lord Kelvin recognised that the energy of the current is mainly supplied by the chemical energy of the reaction, but the exact way in which the potential difference comes into being was not clear, and experiments had shown that potential differences can arise between solutions of electrolytes of different concentrations or different compositions, when no metallic contacts or chemical action can intervene.

The solution of the problems was given by Nernst in publications [2] in 1888—89 on "the electromotive activity of ions" and, although his theories have been modified and extended, the daily work of practical electrochemists is still based on equations first obtained by him. Every pH measurement rests on them, and the determination of pH by indicators and the use of buffer solutions were developed at his suggestion in 1903.[3]

He began by applying Fick's general theory of diffusion to an electrolyte. In solutions of different concentrations in contact, the driving force on each ion was assumed to be proportional to the osmotic pressure gradient, $-\mathrm{d}p/\mathrm{d}x$. The moving ion experiences a large frictional resistance, which may be taken as the force required to move a g.-ion with unit velocity, the mobility $U$ or $V$ of the cation or anion being the reciprocal of this force, or the velocity per unit force. The diffusate in unit time is equal to the number of ions multiplied by the force on each and the speed with which it moves. For univalent ions of concentration $c$, the force per mole is $(1/c)(\mathrm{d}p/\mathrm{d}x)$, and the diffusates through a cross-section $q$ due to the osmotic pressure gradient, in a time $\mathrm{d}t$, are:

$$-Uq(\mathrm{d}p/\mathrm{d}x)\mathrm{d}t \text{ and } -Vq(\mathrm{d}p/\mathrm{d}x)\mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The ions moving with different velocities for a very short time set up electrostatic forces which equalise the velocities, and if $\phi$ is the potential and $-\mathrm{d}\phi/\mathrm{d}x$ the potential gradient, the diffusates due to the electrostatic forces are:

$$-Ucq(\mathrm{d}\phi/\mathrm{d}x)\mathrm{d}t \text{ and } +Vcq(\mathrm{d}\phi/\mathrm{d}x)\mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[2] *Z. physikal. Chem.*, 1888, **2**, 613; 1889, **4**, 129.

[3] Salessky, *Z. Elektrochem.*, 1904, **10**, 204; Fels, *ibid.*, p. 208. The phosphate buffer was simultaneously used by Szily (see Friedenthal, *ibid.*, p. 113; Salm, *ibid.*, p. 341). The name pH for $-\log [H^+]$ was proposed by Sörensen in 1909.

Since the ions now move with the same speed, the joint action of the osmotic pressure and potential gradients gives a diffusate :

$$dS = -Uqdt[dp/dx + c(d\phi/dx)] = -Vqdt[(dp/dx) - c(d\phi/dx)] \quad . \quad . \quad . \quad (3)$$

By comparing this with Fick's law, containing the diffusion coefficient $D$ :

$$dS = -Dq(dc/dx)dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

putting $p = cRT$, and eliminating $d\phi/dx$, it follows that :

$$D = RT \, . \, 2UV/(V + U) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By solving (3) for $d\phi/dx$ :

$$d\phi/dx = (V - U)/(V + U) \, . \, (1/c)(dp/dx) = RT(V - U)/(V + U) \, . \, (d \ln c/dx) \quad (6)$$

and by integration :

$$\phi_2 - \phi_1 = e = (V - U)/(V + U) \, . \, RT \ln (c_2/c_1) \quad . \quad . \quad . \quad . \quad (7)$$

where $e$ is the potential difference between the solutions ($c_2 > c_1$), the sign giving the charge on the concentrated solution. A simple thermodynamic deduction of (7) was also given by Nernst.

The case of solutions of different electrolytes was not worked out (it was treated later by Planck), but Nernst proposed a " principle of superposition," according to which the potential difference between two solutions depends only on the ratio of the concentrations, that between 0·01N-potassium chloride and 0·01N-hydrochloric acid being the same as that between 0·1N-potassium chloride and 0·1N-hydrochloric acid. All these results were confirmed by experiments. Nernst [4] pointed out that liquid contact potentials give an experimental proof of the existence of free ions in solutions.

Nernst later suggested [5] that a liquid contact potential could be eliminated by adding an indifferent electrolyte (potassium nitrate or acetate) at the same concentration on both sides, but Tower's method of the salt bridge [6] is the one now mostly used.

Nernst's theory of the production of galvanic current was developed as follows. Metals go into solution only as positive ions. The tendency of a metal to go into solution may be pictured as a " solution pressure," which is opposed by the osmotic pressure of its ions in the solution, tending to deposit them on the metal electrode. The solution acquires a positive and the metal a negative charge, and the equilibrium of the solution pressure and osmotic pressure corresponds with a potential difference $e$ between the electrode and the solution. If the metal has a very small solution pressure, ions will be deposited on it from solution, giving the electrode a positive charge and leaving the solution negatively charged. If the solution pressure and osmotic pressure are equal, there is no tendency for metal to pass into solution or for ions to be deposited on the metal, and the potential difference $e$ is zero.

Let $A$ be the work gained when 1 electrochemical equivalent of electrode metal passes isothermally and reversibly into a solution of its ions of osmotic pressure $p$. The electrical work is :

$$A = e$$

If $p$ becomes $p + dp$, $A$ becomes $A + dA$, and $e$ becomes $e + de$, and $dA$ is the work done in bringing 1 electrochemical equivalent of ion from the pressure $p + dp$ to the pressure $p$. This is $pdv$, where $dv$ is the increase in volume of the solution when $p + dp$ changes to $p$. Hence :

$$de = pdv = -(RT/p)dp,$$

where $pv = RT$, $R$ being the gas constant per electrochemical equivalent. By integration :

$$e = RT \ln (P/p) = RT \ln (C/c)$$

where $c = p/RT$ is the concentration, and $P$ and $C$ are integration constants. Since $e = 0$ when $p = P$, this is the solution pressure. If $e_0$ is the potential difference in a solution of unit concentration :

$$e = e_0 - RT \ln c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and if $e_1$ is the potential of a standard electrode and $e'$ the contact potential between the two solutions, the electrode potential referred to the standard electrode is :

$$e = e_0 - (e_1 + e') - RT \ln c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Put $e_1 = 0$, then if $e'$ is eliminated, the equation (8) is recovered. Nernst [7] in 1900 proposed to

[4] *Chem. Zentr.*, 1890, **60**, 145.
[5] Bugarsky, *Z. anorg. Chem.*, 1897, **14**, 145.
[6] Tower, *Z. physikal. Chem.*, 1895, **18**, 17; 1896, **20**, 198; cf. Negbaur, *Ann. Physik*, 1894, **44**, 737.
[7] *Z. Elektrochem.*, 1900, **7**, 253.

take the hydrogen electrode as the standard electrode. With small adjustments by means of activities, these equations are still in use.

Others of Nernst's researches on electrochemistry are on decomposition potentials, the residual current, a theory of contact potentials, the theory of the lead accumulator, the determination of the ionic product of water by the acid–alkali cell, the electromotive activity and deposition of alloys, and the diffusion of electrolytically deposited hydrogen through platinum and palladium, and the proof that a palladium electrode becomes charged with hydrogen in a solution of a reducing agent, so behaving as a hydrogen electrode. He devised a simple apparatus for demonstrating the migration of a coloured ion in electrolysis by the moving-boundary method, and an apparatus for measuring transport numbers by the Hittorf method. He proposed [8] a method for measuring the hydration of ions from transport measurements in solutions containing an indifferent solute. A Wheatstone bridge with condensers in the ratio arms was used to measure the internal resistance of a cell.

Nernst's theory of the dropping mercury electrode was based on that of a concentration cell, and Palmaer proved experimentally that the mercury drops cause changes of concentration of mercury ions in solution. In a solution containing only a very small concentration of mercury ions, corresponding with the solution pressure, the dropping and the stationary mercury should have the same potential, and, by combining the stationary electrode with a calomel electrode, the potential of the latter could be found. Palmaer prepared such a solution, and found $+0{\cdot}52$ v for the absolute potential of the normal calomel electrode.

Nernst,[9] who was always receptive of new ideas and discoveries, used the atomistic theory of electricity, calling the unit charges positive and negative electrons, $\oplus$ and $\ominus$, which combine with atoms or radicals to form ions. The negative electron might exist momentarily free in solutions during such reversible changes as $Cl + Br^- \rightleftharpoons Cl^- + Br$. The positive electron would be isolated with difficulty, because of its great affinity for material particles. Nernst and Moers (1920) first recognised the existence of the negative hydrogen ion, $H^-$, and showed that hydrogen tends to move to the anode in the electrolysis of fused lithium hydride, $Li^+H^-$.

Nernst and Riesenfeld (1901) investigated the electrolytic phenomena at the boundary of two solvents, and Nernst (1908) proposed a quantitative theory of nerve stimulation. The electrical stimulus was assumed to depend on changes of concentration of an electrolyte at the boundary between protoplasm and the cell liquid, in which the ions have different mobilities. With alternating currents of high frequency and small intensity, the concentration changes are compensated by diffusion from the solution, and no physiological effect results. High-frequency currents are painless. With lower frequency and higher intensity, the concentration changes are appreciable and there is nerve stimulation. The equations were confirmed by experiments with frog muscle, the oldest detector of galvanic phenomena.

The Nernst method (1894) for measuring the dielectric constants of liquids by a Wheatstone bridge circuit with condensers in the bridge arms, the conductivity of the liquid being compensated, is a good example of his skill in devising apparatus, and has been largely used. He was the first to show,[10] in detail, that solvents of high dielectric constant should promote ionisation, this being independently but briefly stated soon afterwards by J. J. Thomson.[11] Nernst pointed out that solvents with great ionising power show a tendency to association, and emphasised that the dielectric constant is not the only property promoting ionisation, since there are specific influences, particularly the association of the ions with the solvent molecules, since ions have a great tendency to form co-ordination compounds. Nernst and Drude showed that an ionised solute causes a contraction of the solvent by electrostriction due to the charged ions, if the dielectric constant of the solvent increases with pressure.

### Theory of solutions

In his theoretical consideration of dilute solutions Nernst followed van't Hoff in starting with the osmotic pressure, pointing out that, although the thermodynamical investigations are all based on the calculation of the maximum work obtained by the addition of the solvent to a solution in various ways, the generalisation of Avogadro's rule by the analogy between gaseous and osmotic pressure provides a simple theoretical explanation of the properties of dilute solutions. His treatment of diffusion was based on osmotic pressure. He described a simple

[8] *Göttingen Nachr.*, 1900, **68**, and papers following this.
[9] "Theoretische Chemie," 4th edn., 1903. The ideas are similar to those later proposed by Ramsay, *J.*, 1908, **93**, 774.
[10] *Göttingen Nachr.*, 1893, 491 (July); *Z. physikal. Chem.*, 1894, **13**, 531.
[11] *Phil. Mag.*, 1893, **36**, 313 (October).

apparatus for demonstrating osmotic pressure and worked out equations for the osmotic pressure in mixed solvents. With Abegg (1894) and with Hausrath (1905) he carried out precision measurements of the freezing points of solutions, the theory of the errors being developed. He pointed out that the method of producing constant temperatures by freezing salt solutions, published by T. W. Richards in 1903, had been published from Nernst's laboratory by Roloff in 1892. He developed the theory of the elevation of boiling point for a volatile solute, considered the determination of molecular weights in dilute solid solutions, and generalised the equations for hydrolysis.

Nernst was responsible for the theory of solubility product [12] (1889), which Ostwald showed in detail could provide a rational foundation for qualitative and quantitative analysis, and in 1891 he generalised the distribution law,[13] which Berthelot and Jungfleisch had found, in 1872, to apply to some solutes but not to others. Nernst showed that the discrepancies are due to the circumstance that the solute has different molecular weights in the two solvents. The results with benzoic acid agreed with the law if it was assumed to exist as double molecules in benzene but single molecules in water. He also took account of the depolymerisation equilibrium by applying the law of mass action. Roloff, at Nernst's suggestion, used the distribution law to demonstrate the presence of the ion $Br_3^-$ in solutions of bromine in potassium bromide solution. Nernst showed that the molecular weight of a solute may be found from its effect in reducing the partial miscibility of ether and water, which may be followed by the freezing point.

The theory of the velocity of heterogeneous reactions developed by Nernst [14] (1904) assumed that equilibrium is practically instantaneously established at the boundary of two phases, and that the measured velocity is determined almost entirely by the rate at which the reactant diffuses to the interface. If the liquid is vigorously stirred, the solution has a constant composition outside a layer of thickness $\delta$ adhering to the solid. If $a$ is the original concentration in the solution, the diffusate to the interface of area $O$ in time $dt$ is :

$$OD(a - x)dt/\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $D$ is the diffusion coefficient. Boguski had found for the solution of marble in acid that the velocity is proportional to the concentration and surface :

$$dx/dt = kO(a - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and from (10) and (11) :

$$k = D/\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Brunner found that the velocity of solution of magnesia is greater in acetic acid, which diffuses more rapidly, than in the stronger benzoic acid, and the phenomenon is essentially physical; it depends on the diffusion coefficient $D$, and the velocity cannot give an order of reaction. Although Nernst's theory does not hold for all heterogeneous reactions, it does seem to apply to the solution of metals in iodine solution and, whereas the results for the velocity of crystallisation from solutions were thought to be in disagreement with the theory, the latest experiments seem to support it.

Nernst attempted [15] (1901) to give a thermodynamic explanation of the failure of Ostwald's dilution law for strong electrolytes, but this difficult problem was solved only later, on the basis of the theory of interionic attraction. He was never convinced of the complete ionisation of electrolytes and some of his last work (1926—28), with Orthmann, on the heats of dilution of very dilute solutions of electrolytes, was interpreted as showing that there is a very small, practically negligible, un-ionised fraction in equilibrium with the ions according to the law of mass action.

Nernst emphasised that colloidal solutions resemble true solutions more than mechanical suspensions, since they have small but measurable diffusivities and freezing-point lowerings, and appreciable osmotic pressures, all methods giving high molecular weights of the same order. He took the side of Ehrlich in his controversy with Arrhenius, who had applied the law of mass action to the combination of toxins and antitoxins, which he regarded as reversible. Nernst considered (1904) that Arrhenius had mistaken very slow changes for equilibrium states. This led to some coolness between the two old friends, which seems to have been put right later. Although it belongs to a rather different field, Nernst's explanation [16] (1910) of the sharp clearing points of liquid crystals on the basis of an extension of Bose's swarm theory, makes use of the

[12] *Z. physikal. Chem.*, 1889, **4**, 372.
[13] *Ibid.*, 1891, **8**, 110.
[14] *Ibid.*, 1904, **47**, 52.
[15] *Ibid.*, 1901, **38**, 487.
[16] *Z. Elektrochem.*, 1910, **16**, 702.

abnormal increase of vapour pressure of very small drops, and hence belongs to surface chemistry. This interesting contribution seems to be imperfectly known and is rarely mentioned.

### Thermodynamics

Nernst's approach to thermodynamics was a simplification of that of Helmholtz. Every spontaneous process when suitably performed can yield work, which is a maximum when the process is conducted reversibly. The second law shows that the maximum work of an isothermal process depends only on the initial and the final state. The work done in a reversible Carnot's cyclic process absorbing a finite amount of heat $Q$ at an absolute temperature $T$ is :

$$\mathrm{d}A = Q(\mathrm{d}T/T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where $T - \mathrm{d}T$ is the lower temperature in the cycle and $Q$ is the latent heat absorbed in the change along the upper isotherm. Let the state of the system be defined by $T$ and any number of variables $x$, such as volume, surface area, or quantity of electricity, such that if $T$ changes but the $x$'s are held constant no work is done ; whilst if $T$ is held constant and $x$ changes by $\mathrm{d}x$ the work $\mathrm{d}A = X\mathrm{d}x$ is done, where $X$ is a generalised force such as pressure, surface tension, or electromotive force. Clapeyron had shown (1834) that the area of a small Carnot cycle, representing the work done, is equal to the area of a cycle formed of the two isothermals and the verticals through $x$, the initial state, and $x + \mathrm{d}x$, the final state. Since the finite process involving the change of $x$ by $\Delta x$ and the absorption of $Q$ is the sum of the upper isotherms of the infinitesimal cycles, equation (13) follows by summation, and applies to each species of $x$. This proof is strict, and is the most direct approach to the formulation.

If $-U$ is the increase of energy in the change along the isotherm $T$, the first law gives :

$$Q = A - U \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and (13) and (14) give : $$A - U = T\,\mathrm{d}A/\mathrm{d}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Equation (15) was extensively used by Nernst. It was first deduced in 1855 by Lord Kelvin,[17] and was used in chemical investigations by Horstmann in 1872. It was derived again by Helmholtz in 1882, who denoted $A$ by $F$ and called it free energy. As far as I know, it was never stated or used by Gibbs, although it is sometimes misnamed " the Gibbs–Helmholtz equation." Nernst attached importance, with stated reasons, to the symbols and signs in his equations ; he was familiar with thermodynamic methods using entropy and chemical potentials, and often restated the results in terms of these functions, at the same time very properly pointing out that they bring nothing fundamentally new into the calculations. Beginners may find it easier to work with the symbol $\Delta$ for finite increments, but Nernst was more in sympathy with the practical electricians, who use Ohm's law in the form $C = E/R$, never symbolise $E$ as a potential difference, and acquire facility in adapting this simple equation to complicated special cases. It will be seen presently that Nernst's formulation leads very directly to his new Heat Theorem.

Lord Kelvin in 1852 had pointed out that every spontaneous change decreases the free energy of a system, and Lord Rayleigh in 1875, and Helmholtz in 1882, applied this principle to chemical reactions. Since a chemical reaction proceeds in the direction of the affinity, the maximum work or decrease of free energy $A$ may be taken as a measure of the affinity.

Helmholtz in 1847, and Lord Kelvin in 1850, had equated the electrical work of a galvanic cell to the heat of reaction, which amounts to equating $A$ to $U$, and Julius Thomsen in 1853, and Berthelot in 1864, had proposed that the heat of reaction should be taken as a measure of the affinity in a chemical change. Thomsen said :

> " Every simple or complex action of a purely chemical nature is accompanied by an evolution of heat,"

and Berthelot that :

> " Every chemical reaction capable of accomplishment without the intervention of preliminary work, and apart from the intervention of energy foreign to the bodies present in the system, is necessarily produced if it evolves heat."

In a later statement of this *principe du travail maximum*,[18] Berthelot limited its application to reactions between solids, in which case it is approximately correct, and said that it would be

[17] *Quart. J. Math.*, 1857, **1**, 57 (dated 1855) ; *Proc. Roy. Soc. Edin.*, 1898, **22**, 126 (deduction without the use of entropy).

[18] " Thermochimie," Paris, 1897, Vol. I, p. 10 *et seq.* At that time the position had been clarified by the publications of Helmholtz.

more exact at low temperatures. Since he defines "chemical heat," to which the principle applies, as that transformable into work, it is really free energy, and the name *travail maximum* was also significant.

Equation (15) shows that the equation :

$$A = U \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

which is equivalent to the Thomsen–Berthelot principle, can, if $\mathrm{d}A/\mathrm{d}T$ remains finite, be symbolically true only at the absolute zero, $T = 0°$, and Ostwald emphasised that the Thomsen–Berthelot principle cannot be a general law. In the early editions of his text-book Nernst had pointed out that, however true this algebra may be, in many cases the direction of reaction does coincide with evolution of heat, and that a law which holds in many cases, but fails in a few cases, is likely to contain some undiscovered truth. In 1907 he said : [19]

> "A long study of this relation in the past has led me to the hypothesis that *we are dealing with a law more or less approximate at ordinary temperatures, but true in the neighbourhood of the absolute zero.*"

He observed that equation (16) follows from (15) also if $\mathrm{d}A/\mathrm{d}T = 0$ whilst $T$ is finite. In 1894 he had found this relation to hold very nearly for the maximum work of dilution of concentrated solutions of sulphuric acid, whilst with dilute solutions $A$ and $U$ are very different. The generalisation of this result, read to the Göttingen Academy on December 23rd, 1905, and published in 1906, is Nernst's new Heat Theorem, sometimes called (and by Nernst himself) the Third Law of Thermodynamics. It states that for reactions between pure solids or liquids, *i.e.*, in condensed systems :

$$\mathrm{Lim}\ (\mathrm{d}A/\mathrm{d}T) = 0 \text{ as } T \longrightarrow 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

He first stated this in the form :

$$\mathrm{Lim}\ (\mathrm{d}A/\mathrm{d}T) = \mathrm{Lim}\ (\mathrm{d}U/\mathrm{d}T) = 0 \text{ as } T \longrightarrow 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

so that the curves representing $A$ and $U$ as functions of $T$ approach and coalesce to a horizontal line from some finite temperature above the absolute zero, the distance from the absolute zero varying for different systems. It is easy to show that (18) is a necessary consequence of (17). From (14) and (15) :

$$\mathrm{d}A/\mathrm{d}T = Q/T = \Delta S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where $\Delta S$ is the increase of entropy, hence (17) may be formulated :

$$\mathrm{Lim}\ \Delta S = 0 \text{ as } T \longrightarrow 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Kirchhoff in 1858 had shown that :

$$\mathrm{d}U/\mathrm{d}T = H_v - h_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where $H_v$ and $h_p$ are the heat capacities at constant volume of the initial and final systems, and hence (21) implies that Joule's extension of the law of Dulong and Petit (that the molecular heat of a solid compound is the sum of the atomic heats) is exactly true at the absolute zero. Planck in 1911 pointed out that (20) is identically true if :

$$\mathrm{Lim}\ S = 0 \text{ as } T \longrightarrow 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

for each reacting solid separately, and since from thermodynamics :

$$T(\mathrm{d}S/\mathrm{d}T)_v = c_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$c_v$ being the specific heat at constant volume, then :

$$\mathrm{Lim}\ c_v = 0 \text{ as } T \longrightarrow 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

This remarkable result was first verified experimentally by Nernst with diamond, as is mentioned later.

In 1912 Nernst showed that the third law can be deduced from the assumption that a body cannot be cooled to the absolute zero by any finite process, but since Einstein was at first unable to accept this deduction it would seem preferable to retain the usual forms (17) or (18).

In his first publication of the Heat Theorem, Nernst expressed $U$ in the form :

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \cdots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

pointing out that, however common it is for mathematicians to use such power series, this may not be the correct form. From 18 and (21) it follows that $\alpha = 0$, and :

$$U = U_0 + \beta T^2 + \gamma T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

[19] "Experimental and Theoretical Applications of Thermodynamics to Chemistry," 1907, 45 (italics in original).

If (15) is written in the form :

$$\mathrm{d}(A/T)/\mathrm{d}T = -U/T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

and $U$ substituted from (26), it follows that :

$$\mathrm{d}(A/T)/\mathrm{d}T = -U_0/T^2 - \beta - \gamma T$$

and by integration :

$$A = U_0 - \beta T^2 - \tfrac{1}{2}\gamma T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

the integration constant, from (17), being zero. The two equations (26) and (28) express the consequences of the Heat Theorem for condensed reactions on the basis of equation (25). The integral of the general equation (27) may be written :

$$A = T\int(U/T^2)\mathrm{d}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

with no integration constant, and any suitable temperature function can replace (25), as was later done when specific heats were represented by the quantum theory. Nothing fundamentally new from the point of view of the Heat Theorem results from this procedure.

Nernst pointed out that Bodländer, following his suggestion, had calculated the solubilities of salts from the heats of formation and the electrolytic decomposition potentials of compounds (*e.g.*, silver iodide) giving solid products. Equation (28) was applied to the calculation of the transition point of sulphur, the dissociation pressures of hydrates, and the electromotive forces of some cells. At the time when it was proposed there was very little quantitative information which could be used as a test of the validity of the Heat Theorem. In the case of the Clark cell, operating at the cryohydric point (when the cell reaction occurs between pure substances), the $A$ and $U$ curves merge into a horizontal line at 150° K, and the Heat Theorem was shown to apply at such quite high temperatures in other condensed reactions. The approximate validity of the Thomsen–Berthelot principle was thus explained. It should not be supposed, however, that (28) is equivalent to (16), since for the reaction :

$$\mathrm{K_4Fe(CN)_6{,}3H_2O = K_4Fe(CN)_6 + 3H_2O(ice)}$$

the $A$ curve rises steadily from 0° K, whilst the $U$ curve sinks, cuts the temperature axis at about 160° K, and then changes in sign, thus contradicting (16).

The equations so far obtained do not apply to gas reactions or reactions in solutions, for which $A$ and $U$ are often widely different. Nernst in 1905 showed, however, that the Heat Theorem can be applied to gas reactions if these are supposed to take place between the vapours of the reacting substances in the solid state at low temperatures, the final equation for the gas reaction being true at any temperature. The deduction was based on equations (26) and (28) and, although it is easily generalised,* I will give it in the original form.

Consider the gas reaction :

$$\mathrm{CO + H_2O = CO_2 + H_2}$$

Let $C_{\mathrm{CO}}$ etc. be the actual concentrations of the reacting gases, $c_{\mathrm{CO}}$ etc. their equilibrium concentrations, $K = c_{\mathrm{CO_2}} \times c_{\mathrm{H_2}}/c_{\mathrm{CO}} \times c_{\mathrm{H_2O}}$ the equilibrium constant, $U$ the heat of reaction (evolved), and $A$ the maximum work. Van't Hoff had shown that :

$$A = \boldsymbol{R}T \ln \frac{C_{\mathrm{CO}} \times C_{\mathrm{H_2O}}}{C_{\mathrm{CO_2}} \times C_{\mathrm{H_2}}} + \boldsymbol{R}T \ln K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

an equation often called the reaction isotherm. Differentiation of (30) and substitution in (15) gives :

$$-U = \boldsymbol{R}T^2 \frac{\mathrm{d} \ln K}{\mathrm{d}T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

an equation also found by van't Hoff, and often called the reaction isochore. With $U$ from (25)—for a gas reaction $\alpha$ is not zero—(31) gives on integration :

$$\ln K = \frac{U_0}{\boldsymbol{R}T} - \frac{\alpha}{\boldsymbol{R}} \ln T - \frac{\beta}{\boldsymbol{R}} T - \frac{\gamma}{2\boldsymbol{R}} T^2 + I \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

If the integration constant $I$ were known, $K$, and hence from (30) $A$, could be calculated, but $I$ cannot be found from the two laws of classical thermodynamics. It can be found from the Nernst Heat Theorem as follows. If all the reacting substances are present as pure solids the Clapeyron–Clausius equation gives for the pressure of the saturated vapour (assumed to be an ideal gas) :

$$\mathrm{d} \ln p/\mathrm{d}T = \lambda/\boldsymbol{R}T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

* See, *e.g.*, Partington, "A Text-Book of Thermodynamics," Constable, London, 1913, p. 491, using chemical potentials and equation (29).

where $\lambda$ is the molar heat of sublimation, which may be expressed in the form :

$$\lambda = \lambda_0 + \alpha_0 T + \beta_0 T^2 + \gamma_0 T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

From (33) and (34), by integration :

$$\ln p = -\frac{\lambda_0}{RT} + \frac{\alpha_0}{R} \ln T + \frac{\beta_0}{R} T + \frac{\gamma_0}{2R} T^2 + i' \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where $i'$ is the integration constant. If $C$ is the concentration, $p = CRT$, and :

$$\ln C = -\frac{\lambda_0}{RT} + \left(\frac{\alpha_0}{R} - 1\right) \ln T + \frac{\beta_0}{R} T + \frac{\gamma_0}{2R} T^2 + i \quad . \quad . \quad . \quad . \quad (36)$$

where $i = i' - \ln R$ is a constant depending only on the chemical composition of the substance, and called by Nernst the *chemical constant*. The value of $C$ given by (36) and that of $K$ given by (32) are substituted in (30) and, since the reaction is ultimately one between pure solids, (28) shows that the coefficient of $T$ in the resulting equation is zero. This gives :

$$I = \Sigma n_1 i_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where $n_1$ is the number of molecules of a reacting substance, and hence the value of $I$ in (32) is known. The case of a heterogeneous reaction follows as usual, the values of $c$ and $i$ vanishing for every solid phase, but the heat of reaction $U$ being that of the complete reaction.

In 1907 Nernst [20] drew attention to some earlier publications of interest. Le Chatelier [21] in 1888, in considering equation (32), had said :

> " It is very probable that the constant of integration [*i.e.*, $I$], like the coefficients of the differential equation [*i.e.* (31)] is a definite function of certain physical properties of the reacting substances. The determination of the nature of this function would lead to a complete knowledge of the laws of equilibrium. It would make it possible to determine *a priori*, independently of any new experimental data, the complete conditions of equilibrium corresponding with any given chemical reaction. The exact nature of this constant has, up to the present, not been determined."

Le Chatelier drew attention to the importance of specific heats and vapour pressures in relation to the equilibrium constant, but added that he had not discovered the relation in question.

T. W. Richards,[22] in what Nernst calls " a very interesting paper " of 1902 on " the relation of changing heat capacity to change of free energy, heat of reaction, change of volume and chemical affinity," drew attention to the relation between the sign and value of $A - U$ and the change of heat capacity ($H_v - h_v$) in a chemical reaction, giving some diagrams for galvanic cells showing the coalescence of the curves of $A$ and $U$ as functions of temperature into horizontal lines below $-200°$ c (the very low temperature is noteworthy). He says, however, that this is " a necessary consequence of the equation of Helmholtz " (*i.e.*, Kelvin's equation 15), in which $A = U$ when $T = 0$. He does not give anything equivalent to equation (18), saying that :

> " On the basis of the present data it is impossible to attempt to calculate the mathematical relation of $\partial U/\partial T$ to $\partial A/\partial T$, or to probe further into the mechanism of the change. When more exact data have been obtained, it may be possible to arrive at more definite conclusions."

Richards at that time reached the conclusion that :

> " In a reaction from which concentration effects have been eliminated, when the total heat capacity remains constant during the reaction, the change of free energy and the heat evolved are constant."

Equation (21) shows that this is equivalent to $dU/dT = 0$, but Richards does not draw attention to this and his paper is quite difficult to follow. A study of it by van't Hoff [23] in 1904 led to a result very different from (18). Eight years after Nernst's publication of the Heat Theorem, Richards [24] claimed that it had been anticipated in his paper of 1902, saying that :

> " All these ideas were afterwards (1906) adopted unchanged by Nernst in his development of the ' Wärmetheorem ' usually named after him."

[20] " Experimental and Theoretical Applications of Thermodynamics to Chemistry," New York, 1907, p. 54.
[21] Recherches expérimentales et théoriques sur les équilibres chimiques, *Ann. Mines*, 1888, **13**, 336, 356.
[22] *Proc. Amer. Acad.*, 1902, **38**, 293.
[23] Boltzmann Festschrift, 1904, 232.
[24] *J. Amer. Chem. Soc.*, 1914, **36**, 2433.

Nernst,[25] who drew attention to his reference to Richards in 1907, which he thought would "avoid superfluous polemics," now felt obliged to "refute the claim made by Richards to my Heat Theorem," which he did in an objective and decisive way; he showed that the results given by Richards would not hold if the $U$ curve has a maximum or a minimum, which in many cases it has. G. N. Lewis,[26] perhaps the most brilliant pupil of Richards, later said very fairly and correctly that:

> "The curves presented by Richards very nearly imply the generalizations which were later embodied in the third law of thermodynamics."

Nernst had also, in 1907, referred to what he calls "the remarkable book" by Haber, pointing out that Haber's equations differ from his. In the English translation of his book,[27] Haber supplied a clear account of the Nernst Heat Theorem, said the conclusions he had drawn from Richards's paper were incompatible with it, and made no claim to have anticipated it. I believe that no valid doubt exists of Nernst's originality and priority in the statement of the new thermodynamic principle.

The values of the chemical constants $i$ may be calculated by means of equations (35) and (36) from the vapour pressure curves, suitably corrected for deviations from the ideal gas state. Since data were mostly lacking at the time, Nernst used some ingenious empirical results. He assumed that: (i) for a gas containing $m$ atoms in the molecule the molar heat $C_p$ near the absolute zero is $3{\cdot}5 + 1{\cdot}5m$; (ii) the atomic heat of a solid element at absolute zero is much lower than the Dulong and Petit value, and may be taken as 1·5, but may be zero; (iii) for evaporation, Young's results give the empirical equation:

$$p(v_g - v_l) = \boldsymbol{R}T(1 - p/p_c),$$

where $v_g$ and $v_l$ are the molar volumes of the vapour and liquid and $p_c$ the critical pressure; (iv) the heat of evaporation is expressible in the form:

$$\lambda = (\lambda_0 + 3{\cdot}5T - \varepsilon T^2)(1 - p/p_c)$$

where $\varepsilon$ is a constant. The Clapeyron–Clausius equation (33) then gives:

$$\ln p = -\frac{\lambda_0}{\boldsymbol{R}T} + \frac{3{\cdot}5}{\boldsymbol{R}} \ln T - \frac{\varepsilon}{\boldsymbol{R}} T + i'$$

Therefore,

$$(i + \ln \boldsymbol{R})/2{\cdot}3023 = \lambda_0/4{\cdot}571T - 1{\cdot}75 \log T + (\varepsilon/4{\cdot}571)T + \log p = C$$

where $C$ is a "conventional chemical constant." For all substances except hydrogen and helium, $C$ may be taken as approximately 3, for hydrogen and helium it is approximately 1·5. For a gas reaction, if $\nu$ is the excess of the number of molecules of the reacting species over the number of molecules of the products, then:

$$n_1A_1 + n_2A_2 + \cdots = n_1'A_1' + \cdots; \quad (n_1 + n_2 + \cdots) - (n_1' + \cdots) = \nu,$$

and if an equilibrium constant is expressed in terms of partial pressures:

$$K' = p_1^{n_1}p_2^{n_2}\cdots/p_1'^{n_1'}\cdots = (\boldsymbol{R}T)^{\nu}/K$$

where $K$ is the equilibrium constant defined as in (30), then:

$$\ln K' = -Q_0/4{\cdot}571T + 1{\cdot}75\nu \log T + (\beta/4{\cdot}571)T + \Sigma n_1C_1$$

where

$$Q = Q_0 + 3{\cdot}5\nu T + \beta T^2$$

is the heat of reaction (evolved) at constant pressure. This equation was used in many interesting calculations. In many cases the term $(\beta/4{\cdot}571)T$ may be neglected and results of significance can then be obtained when full experimental data are unknown. Nernst found some empirical equations for $C$, *viz.*:

$$C = 1{\cdot}1a = 0{\cdot}14(\lambda/T_b),$$

where $a$ is the constant of the van der Waals vapour-pressure equation:

$$\log (p/p_c) = a(T_c/T - 1)$$

[25] "The New Heat Theorem," 1926, p. 228.

[26] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," New York, 1923, p. 437.

[27] "Thermodynamics of Technical Gas Reactions," transl. by A. B. Lamb (from the German edition of 1905), 1908; in "The New Heat Theorem," 1923, p. 227, Nernst calls this an "excellent book."

and $\lambda/T_b$ is the Trouton coefficient. He showed that the Trouton coefficient is not a true constant, but for substances of low and high boiling point is given by :

$$\lambda/T_b = 9{\cdot}5 \log T_b - 0{\cdot}007T_b$$

Over a restricted range of temperature a similar relation applies to reactions of dissociation in condensed systems, where if $T_1$ is the temperature at which the dissociation pressure is atmospheric :

$$Q_p/T_1 = \text{const.} = 34$$

a result found empirically by Matignon (1899).

A number of interesting calculations showed that the above equations could give very useful information in many regions, and when experimental data were available, quite good agreement was found with the calculations. Many of the data needed, such as the specific heats of gases and of solids at high and low temperatures, vapour pressures at low temperatures, equilibrium constants of homogeneous and heterogeneous reactions (especially at high temperatures), and electromotive forces, were then unknown.

While still in Göttingen Nernst had begun work on gaseous equilibria at high temperatures. This work was in a sense an outcome of the Nernst lamp. The proceeds from this, mentioned on p. 2855, enabled Nernst to become a pioneer motorist. This aroused his interest in the chemical reactions in the internal combustion engine. The early work of Ste. Claire Deville had shown that the reactions $2H_2 + O_2 \rightleftharpoons 2H_2O$ and $2CO + O_2 \rightleftharpoons 2CO_2$ are incomplete at high temperatures and reach equilibria. In 1903 Nernst had made use of a cylinder of nitrous oxide to enrich the explosive mixture in the engine cylinders and thence to obtain increased power on hill climbs, and very soon he took up in Göttingen the study of the steam and carbon dioxide equilibria at high temperatures, very ingenious experimental methods being applied in association with von Wartenberg. The results of this work and other investigations of equilibria at high temperatures made in Berlin were at the time very significant and valuable, and provided new data in chemical thermodynamics.

The physical chemist is at some disadvantage, compared with the organic chemist, since new compounds remain, but new measurements soon give way to newer, and sometimes better, ones. The pioneering investigations are soon forgotten, and results which in their time were highly important and significant are amplified and revised by later workers, who not infrequently reap the benefit of newer techniques which make their task much easier than that of the earlier pioneer experimenters, whose contributions to science tend to be overlooked. In fairness to Nernst and his associates, it should be emphasised that they enriched chemical thermodynamics with a substantial fund of new data of a kind then almost completely lacking. It will be possible only to mention some of this work in outline.

Vapour densitities were measured in a small iridium Victor Meyer apparatus heated in an iridium tube furnace to over 2000° c, quantities of about 0·001 mg. being weighed in an ingenious microbalance devised by Nernst. The principle of Deville's hot and cold tube was used to measure the dissociation of steam and carbon dioxide, and the velocity of formation and decomposition of nitric oxide. Dissociation was measured by heating a platinum wire in steam, and heating hydrogen sulphide in a platinum bulb, through which the hydrogen diffused. This work was done in collaboration with von Wartenberg, Löwenstein, Preuner, Jellinek, and Langmuir. The explosion-pressure method was used in a much improved form by Pier, Bjerrum, and Siegel to measure the dissociation and mean specific heats of gases at high temperatures. Nernst (1904) pointed out that the dissociation of a gas could be measured from the abnormal increase in thermal conductivity with temperature. Langmuir afterwards discovered atomic hydrogen by this method. From the results for the dissociation of steam, Nernst and von Wartenberg calculated the electromotive force of the Groves gas battery, in which hydrogen and oxygen are in contact with platinum electrodes in aqueous solutions, finding 1·232 v at 17°. The observed value is 1·15 v, but this is really the potential of an oxide of platinum. Brönsted measured the electromotive force of the cell $Pt,H_2/NaOH$ aq./HgO,Hg and by calculating the oxygen pressure by extrapolation of the dissociation pressures of mercuric oxide at higher temperatures, calculated the electromotive force at 17° for hydrogen and oxygen at atmospheric pressure as 1·234 v, in good agreement with that calculated by Nernst and von Wartenberg.

The high-temperature equilibrium work involved the use of optical pyrometry and the technique of this was carefully studied. By combining results from such measurements with those found from electromotive forces, many other equilibrium constants, such as that of the

Deacon process, could be calculated. Only one investigation, that of the synthetic-ammonia equilibrium, will be mentioned, on account of its historical interest.

In 1905 Haber and van Oordt had measured the yields of ammonia at atmospheric pressure, but these are so small that a good result could hardly be expected. Nernst found that they were not in agreement with those calculated from the Heat Theorem, and he began work on ammonia synthesis. To obtain higher yields and greater velocities, he worked under pressure, up to about 50 atm., using glass tubes. This work, by Nernst and his pupils Jellinek and Jost, was the first carried out for the reaction under pressure, and the first to give reasonably accurate results. The results differed appreciably from those found by Haber and van Oordt, and in 1906 Nernst, informing Haber of this, suggested that he should make experiments at higher pressures. For some reason, Haber was disinclined to accept this suggestion, and in 1907, in a discussion of Nernst's paper, he maintained this attitude, at the same time clearly if not openly implying that Nernst's method was faulty and that his results were inaccurate. Newer measurements with Le Rossignol had, he said, given results closer to Nernst's but still different from them. They were still based on work at atmospheric pressure, with indicators to detect the small traces of ammonia formed. The conclusion of the discussion by Nernst [28] is quite objective, even if rather sharply worded. He had a great admiration for Haber's work, which he more than once put on record, but he always reacted sharply to adverse criticism of the accuracy of his own, particularly if it was not supported by experiments made under the same conditions as he had used. It was not until 1908 that Le Rossignol, in Haber's laboratory, reported measurements made under pressure. The later history of ammonia synthesis does not concern us, but it may be mentioned that the earlier values of the heat of reaction and the specific heats were later found to be incorrect and, on the theoretical side, the then unknown existence of ortho- and para-hydrogen introduces a complication into calculations of equilibria involving hydrogen. Nernst gave a favourable report on Haber's patents concerned with the catalyst to the Badische Anilin A.-G. but he did not patent his own contribution of the use of high pressures, since he was assured by Duisberg that the use of such pressures was impossible in technical practice. The difficulties were, in fact, afterwards overcome by Bosch, and this unexpected development very naturally caused Nernst some annoyance.

In 1905 my teacher, Professor H. B. Dixon, read to the German Chemical Society an account of what Nernst called his " outstanding experimental researches " on the detonation wave. In a lecture in that year, and in a pamphlet on the internal combustion engine, Nernst gave a clear account of this work, suggesting, however, that Dixon's molecular theory could be replaced by one based on hydrodynamics. The theory of the detonation wave, involving discontinuities in the solution of the differential equations, had proved to be very difficult, but the notable theoretical investigations of D. L. Chapman,[29] undertaken at Dixon's suggestion, were later extended by R. Becker,[30] who gave a satisfactory account of the phenomena on the lines of hydrodynamics, as suggested by Nernst, pointing out, however, that Dixon's fundamental idea that the molecules on the hot side of the wave front shoot into the unburnt gas, and by their collision with cold molecules bring these immediately into chemical reaction, is essentially correct.

Nernst also initiated some experiments on the ignition points of gases by adiabatic compression, but the results found by Falk [31] in his laboratory were shown by Dixon and by Tizard to be vitiated by pre-flame combustion whilst the gases are being compressed, and the conclusion that the mixture $H_2 + O_2$ has the lowest ignition temperature is incorrect. This was later confirmed in Nernst's laboratory by Cassel.[32]

It remains to say something about the Nernst Heat Theorem (the third law of thermodynamics) in relation to the two older laws. Maxwell had pointed out that the first law of thermodynamics, the law of conservation of energy, seemed to hold without exception, whilst the second law would fail in principle if heat is resolved into molecular motion, since if individual molecules are considered, processes violating the second law are easily imagined. Nowadays, the measured change of mass with velocity of particles accelerated in the cyclotron suggests that the laws of conservation of mass and energy do not hold separately, but survive only in a combined form. The second law of thermodynamics, on the other hand, seems to have

[28] *Z. Elektrochem.*, 1907, **13**, 521; " Theoretical Chemistry," 1923, 758; " The New Heat Theorem," 1926, 274.
[29] *Phil. Mag.*, 1899, **47**, 90.
[30] *Z. Physik*, 1922, **8**, 321.
[31] *J. Amer. Chem. Soc.*, 1906, **28**, 1517.
[32] *Ann. Physik*, 1916, **51**, 685; when Cassel began his work he was unaware of Dixon's results, which I mentioned to him.

maintained its integrity in all experimentally attainable conditions. The third law, like the second, rests on a statistical basis, applying to a large number of individuals, but cases in which it fails, small in number, are experimentally realisable.

In solid carbon monoxide and nitrous oxide near the absolute zero, the molecules are not all aligned in the same way and do not, in a reasonable time, take up a position of maximum order, all pointing in the same direction. The solids have, therefore, a positive residual entropy. Solid hydrogen, again, is a mixture of ortho- and para-hydrogen, the transition into para-hydrogen being incomplete. Some have thought that the third law should be limited to perfect crystals, but it seems that the only sure criterion of a perfect crystal is that it follows the third law, and Nernst always maintained that the law applies to liquids. According to Mayer and Mayer,[33] the most general statement of the third law (if such is possible) is of no great interest or value to an experimenter; if there is a zero-point entropy it is impossible to give general directions for its experimental determination; and whatever difficulties there may be in giving at the same time a strict and also experimentally useful statement of the third law, its value must not be underestimated.

Some experiments by Gibson and Giauque,[34] often quoted as indicating a failure of the Nernst Heat Theorem, are in reality indecisive. They were supposed to indicate a finite entropy for a glassy solid at the absolute zero, but this does not follow from them except by an inadmissible extrapolation, and the suggestion made by Simon [35] (who at that time was working in Nernst's former laboratory in Berlin), that specific-heat measurements made rapidly in an ordinary vacuum-calorimeter are vitiated by a very slow adjustment of the glass to an equilibrium state, has been shown to be correct.

The chemical constant $i$ was calculated for a monatomic gas from statistical principles by Sackur (1911—13) and Tetrode (1912) by the equation:

$$i = \ln (2\pi m)^{3/2} \boldsymbol{k}^{5/2}/\boldsymbol{h}^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where $m$ is the mass of the atom, $\boldsymbol{k}$ is Boltzmann's constant, and $\boldsymbol{h}$ is Planck's constant. Nernst found fairly good agreement of this equation with the values of $i$ obtained from vapour-pressure measurements with mercury and argon, but in other cases there was disagreement. It is now known that the expression after the logarithm should be multiplied by a statistical weight $g$, which is unity for argon and mercury, and also zinc vapour, but 2 for sodium, potassium, and thallium vapours, and this was confirmed experimentally by Egerton. A supposed difference between chemical constants found from vapour pressures and those calculated from equilibrium measurements, suggested by Eucken, was afterwards shown to be due to experimental errors.

In modern thermodynamics little use is made of chemical constants. The entropy is calculated from heat capacities and other thermal data by well-known methods and, since it is related to the maximum work and heat of reaction by the equations (15) and (19), *viz.*:

$$A - U = T(\mathrm{d}A/\mathrm{d}T), \text{ and } \mathrm{d}A/\mathrm{d}T = Q/T = \Delta S$$

It follows that:

$$A = U + T\Delta S,$$

and, when $A$ is known, the equilibrium constant can be calculated by van't Hoff's equation (30). Such calculations are superior to Nernst's method when experimental data are available, but they are, of course, only another way of using the Nernst Heat Theorem, and have no theoretical basis apart from it. They offer nothing fundamentally new but are, as it were, a praiseworthy improved method of book-keeping. They require experimentally determined specific heats at very low temperatures, and in this field Nernst was also a pioneer.

### The solid state

The experiments of Tilden and Dewar had shown that atomic heats fall notably below the Dulong and Petit value at the temperatures of liquid air and liquid hydrogen, but they gave only mean values over a large range of temperature. Nernst, Koref, and Lindemann (1910) * greatly improved the experimental method by introducing a new calorimeter, which consisted of a copper block inside a Dewar vessel. The block was provided with thermocouples and the substance, contained in a silver vessel and strongly cooled, was dropped into a cavity in the

[33] "Statistical Mechanics," New York, 1940, p. 103. Older opinions, such as that of Fowler and Stern, *Rev. Mod. Phys.*, 1932, **4**, 707, must now be regarded as untenable.

[34] *J. Amer. Chem. Soc.*, 1923, **45**, 93.

[35] *Z. anorg. Chem.*, 1931, **203**, 219; Obald and Newton, *J. Amer. Chem. Soc.*, 1937, **59**, 2495.

* A summary of the work described in this section, with references to publications, is given in Nernst's book, "The New Heat Theorem," 1926.

block. This apparatus gave a mean specific heat over an interval of temperature. A new vacuum-calorimeter, developed by Nernst and Eucken, consisted of a metal cylinder, or a sealed metal canister, containing the substance with some air or hydrogen (a good conductor of heat) and wrapped with a spiral of platinum or lead wire to serve at the same time as a heater and as a resistance thermometer. The unit was suspended by fine leading wires inside a glass jacket containing hydrogen and immersed in liquid air or liquid hydrogen, which could be boiled under low pressure. When the block had cooled to the temperature of the bath, the hydrogen gas was pumped out so as to establish a good vacuum. A measured amount of electrical energy was supplied to the spiral of wire and the rise in temperature measured. This gave the true specific heat over a small interval of temperature. Nernst and Schwers also used a copper canister with a thermocouple having one junction in a block of lead, the temperature of which remained nearly constant. Much work was carried out on the methods of temperature measurement. The vacuum-calorimeter has been improved and is now extensively used in low-temperature work.

Nernst's results showed that with some solids, such as lead, the specific heat falls only slowly with temperature until very low temperatures are reached, whilst with others, such as copper and aluminium, the specific heat falls more rapidly. In the case of diamond, the atomic heat of which is notably below the Dulong and Petit value of 6 g.-cal. at room temperature, the atomic heat fell to zero at 50° K. Nernst, with F. A. Lindemann (now Lord Cherwell) and Koref, made many measurements of specific heats of solids at low temperatures, and these were the first to give serviceable results.

Einstein in 1907 had extended Planck's quantum theory of radiation to monatomic solids. The classical theory, given by Boltzmann, assumed that the atoms in a solid are vibrating with simple harmonic motion, and that their kinetic energy at any temperature is the same as that of atoms of a monatomic gas. The averate kinetic and potential energies of a harmonic oscillator are equal, and the sum is $3\boldsymbol{R}T$ per g.-atom, hence the atomic heat at constant volume is $3\boldsymbol{R}$ or 6 g.-cal. at all temperatures, which is the Dulong and Petit value. According to Einstein, however, the atoms in a solid cannot take up energy continuously but only in quanta, $\boldsymbol{h}\nu$, where $\boldsymbol{h}$ is Planck's constant and $\nu$ the characteristic frequency of vibration of the atom. The energy between two quanta taken up is missing, and the atomic heat is thus smaller than the classical value, which assumes continuous absorption. If the quantum is small, as with lead, the missing gaps are small and the value of the atomic heat is near 6 g.-cal.; with large quanta, as with aluminium, the gaps are large, and the atomic heat is much lower than this value. The quantitative value is easily found. I will give the calculation according to D. L. Chapman.[36] Suppose the linear oscillators of frequency $\nu$ are gas molecules A, the energy being quantised and having the values 0, $\boldsymbol{h}\nu$, $2\boldsymbol{h}\nu$, $3\boldsymbol{h}\nu \cdots$, $n\boldsymbol{h}\nu$. If the increase of energy is identified with a heat of reaction according to the equation :

$$\mathrm{A}_n = \mathrm{A}_0 + n\boldsymbol{h}\nu$$

and if $N_0, N_1, \cdots, N_E$ are the numbers of oscillators with energies $0, 1, \cdots, E = n\boldsymbol{h}\nu$, van't Hoff's equation (31) gives :

$$\mathrm{d} \ln (N_E/N_0) = n\boldsymbol{h}\nu/\boldsymbol{k}T^2,$$

where $\boldsymbol{k} = \boldsymbol{R}/\boldsymbol{N}$, is Boltzmann's constant, the equilibrium constant being $K = N_E/N_0$. If $C$ is an integration constant and $\boldsymbol{h}\nu/\boldsymbol{k}T = x$, then :

$$N_E = CN_0\mathrm{e}^{-nx}$$

and the average energy of a linear oscillator, after dividing out $CN_0$, is :

$$(\boldsymbol{h}\nu \,.\, \mathrm{e}^{-x} + 2\boldsymbol{h}\nu \,.\, \mathrm{e}^{-2x} + 3\boldsymbol{h}\nu \,.\, \mathrm{e}^{-3x} + \cdots)/(1 + \mathrm{e}^{-x} + \mathrm{e}^{-2x} + \mathrm{e}^{-3x} + \cdots) = \boldsymbol{h}\nu/(\mathrm{e}^{x} - 1) \quad . \quad . \quad (38)$$

the last step being an ordinary long division. The energy of an atom in the solid, Einstein assumed, is equal to that of three linear oscillators at right angles, or per g.-atom the energy is :

$$E = 3\boldsymbol{N}\boldsymbol{h}\nu/(\mathrm{e}^{x} - 1) = 3\boldsymbol{R}\beta\nu/(\mathrm{e}^{\beta\nu/T} - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where $\beta = \boldsymbol{h}/\boldsymbol{k}$. Differentiate with respect to $T$, and the atomic heat at constant volume becomes :

$$C_v = \mathrm{d}E/\mathrm{d}T = 3\boldsymbol{R}(\beta\nu/T)^2\mathrm{e}^{\beta\nu/T}/(\mathrm{e}^{\beta\nu/T} - 1)^2 \quad . \quad . \quad . \quad . \quad . \quad (40)$$

[36] *Ann. Reports*, 1914, **11**, 3.

which is Einstein's equation.* Observed values of $C_p$ may be converted into $C_v$ by a formula given by Nernst and Lindemann:

$$C_p = C_v + 0{\cdot}0214C_p^2T/T_m$$

where $T_m$ is the melting point. The experiments in Nernst's laboratory showed that the observed atomic heats fall off less rapidly at low temperatures than Einstein's formula requires; for example with copper:

| | | | |
|---|---|---|---|
| $T$ (°K) | 88 | 33·4 | 22·5 |
| $C_v$, obs. | 3·38 | 0·538 | 0·223 |
| $C_v$, calc. | 3·31 | 0·234 | 0·023 |

Nernst and Lindemann (1911) found that the experimental value could be represented by a simple and elegant formula which consists of a sum of half the Einstein values with the frequencies $\nu$ and $\nu/2$, so that only one frquency $\nu$ is still required:

$$C_v = \frac{3}{2}\boldsymbol{R}\left\{\left(\frac{\beta\nu}{T}\right)^2\frac{e^{\beta\nu/T}}{(e^{\beta\nu/T}-1)^2} + \left(\frac{\beta\nu}{2T}\right)^2\frac{e^{\beta\nu/2T}}{(e^{\beta\nu/2T}-1)^2}\right\} \quad . \quad . \quad . \quad . \quad (41)$$

Thus, for $\frac{1}{2}$KCl, by using the value $\beta\nu = 218$ found experimentally by the optical method of residual rays:

| | | | | | |
|---|---|---|---|---|---|
| $T$ (°K) | 331 | 86 | 52·8 | 30·1 | 22·8 |
| $C_v$, obs. | 6·16 | 4·36 | 2·80 | 0·98 | 0·58 |
| $C_v$, N.L. | 6·06 | 4·43 | 2·97 | 1·23 | 0·61 |
| $C_v$, E. | 5·90 | 3·54 | 1·70 | 0·235 | 0·039 |

A theoretical equation giving results as good as those from the Nernst–Lindemann equation was deduced by Debye (1912). He identified the heat content of a solid with the energy of short elastic waves of length still large compared with the distance between the atoms. There is now a spectrum of frequencies terminated by a frequency $\nu_m$ imposed by the atomic structure. The elastic solid containing $\boldsymbol{N}$ atoms was treated as a continuum and the ordinary theory of elasticity gives for the number of vibrations between frequencies $\nu$ and $\nu + d\nu$:

$$(9\boldsymbol{N}\nu^2/\nu_m^3)d\nu$$

Each vibration is given the energy according to Einstein's equation (38). By integration:

$$E = \frac{9\boldsymbol{R}}{3}\int_0^{\nu_m}\frac{\beta\nu^3}{e^{\beta\nu/T}-1}\,d\nu = 9\boldsymbol{R}T\left(\frac{T}{\beta\nu}\right)^3\int_0^{\beta\nu/T}\frac{y^3dy}{e^y-1} \quad . \quad . \quad . \quad . \quad (42)$$

where $y$ is the variable in the definite integral. This may be integrated in series. At very low temperatures:

$$E = aT^4;\ C_v = 4aT^3;\ a = \tfrac{3}{5}\pi^4\boldsymbol{R}/(\beta\nu_m)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

where $a$ is a constant. The Debye equation gives good results at low temperatures, as is seen from the results of Nernst and Schwers and of Onnes and Keesom:

| Copper, $\beta\nu_m = 323{\cdot}5$ | | | Lead, $\beta\nu_m = 88$ | | |
|---|---|---|---|---|---|
| $T$ (°K) | $C_v$, obs. | $C_v$, calc. | $T$ (°K) | $C_v$, obs. | $C_v$, calc. |
| 15·24 | 0·0491 | 0·0486 | 15·98 | 1·87 | 1·87 |
| 18·03 | 0·0792 | 0·0804 | 22·4 | 3·00 | 3·06 |
| 19·58 | 0·1010 | 0·1030 | 30·24 | 4·06 | 4·03 |
| 21·50 | 0·1410 | 0·1365 | 47·6 | 5·07 | 5·04 |

In the case of compounds, Nernst suggested that $C_v$ is the sum of a Debye function for the whole molecule and of Einstein functions for the separate atoms, each having a characteristic frequency, and this has a theoretical foundation. The extrapolation of specific heats to absolute zero from the lowest experimental temperature can be carried out by the Debye $T^3$-formula, which is now generally used in calculating the entropies, the region below the lowest experimental temperature being supplied by the formula.

The quantum theory of the specific heats of gases was opened out by Nernst [36] (1911). He assumed that the vibrational energy of gas molecules is represented by Einstein's formula (38), and that the rotational energy may be represented by the same equation with a frequency proportional to the square-root of the absolute temperature, as on the classical theory. He recognised that at low temperatures not only the vibrational energy, if present, but also the rotational energy, will approach zero, and he predicted that the rotational energy of hydrogen,

* A zero-point energy $\frac{1}{2}\boldsymbol{h}\nu$ should be included in (38), but this disappears in the differentiation.

[36] *Z. Elektrochem.*, 1911, **17**, 265.

which has an abnormally low molecular heat even at room temperature, should vanish at the temperature of liquid hydrogen. The value of $C_v$ for hydrogen should then become 3 g.-cal., the same as that of a monatomic gas. This was verified by Eucken with compressed hydrogen in a small steel vacuum-calorimeter. At low temperatures the heat capacity of the metal is small, and that of the gas can be measured with fair accuracy. The correct theory of the rotational energy of gas molecules was closely approached by Bjerrum (1912), who related it to the absorption in the long infra-red, but it was only after the development of wave mechanics that the accurate equation for the specific heat of hydrogen was obtained. It involves the two kinds of hydrogen molecules, ortho- and para-hydrogen.

Nernst later extended the Heat Theorem to gases at low temperatures, but his equations involved an error pointed out by Bennewitz. The quantum theory of gases is a little more complicated than Nernst suspected, since it follows one of two newer types of statistics, but the result, that the specific heat should vanish at the absolute zero, comes out as Nernst supposed. Ordinary gases could not exist at a temperature low enough to show a deviation from Maxwell–Boltzmann statistics (which itself is only an approximation), but electrons, which obey Pauli–Fermi statistics, should, on account of their very small mass, have only very little energy even at room temperature; this explains why Dulong and Petit's law, applying as it does to the ponderable positive ions, is so nearly obeyed by metals, the electrons contributing practically nothing to the energy. At very low temperatures, where the heat content of the ponderable ions has sunk to a very low value, the small specific heat of the electrons becomes appreciable, since it is proportional to the absolute temperature $T$, not to $T^3$.

It should be mentioned that the frequency used in the specific heat equations may be determined, not only by the optical residual ray method (which can be used only with ionic salts), but also from the compressibility or, as Lindemann showed, from the melting point.

Some important consequences of the Heat Theorem, pointed out by Nernst,[37] follow very simply from equation (20), Lim $\Delta S = 0$ as $T \longrightarrow 0$. Clapeyron's equation for the latent heat of expansion is :

$$l_v = T(\mathrm{d}p/\mathrm{d}T)_v$$

hence : $$\text{Lim } (l_v/T) = \text{Lim } (\mathrm{d}p/\mathrm{d}T)_v = 0 \text{ as } T \longrightarrow 0$$

Since $(\mathrm{d}p/\mathrm{d}T)_v = -(\mathrm{d}p/\mathrm{d}v)_T(\mathrm{d}v/\mathrm{d}T)_p$, if $(\mathrm{d}p/\mathrm{d}v)_T$ is finite :

$$\text{Lim } (\mathrm{d}v/\mathrm{d}T)_p = 0 \text{ as } T \longrightarrow 0$$

The latent heat of extension of a liquid film is :

$$l_A = -T(\mathrm{d}\sigma/\mathrm{d}T),$$

where $\sigma$ is the surface tension ; hence :

$$\text{Lim } (-l_A/T) = \text{Lim } (\mathrm{d}\sigma/\mathrm{d}T) = 0 \text{ as } T \longrightarrow 0$$

The magnetisation of a paramagnetic substance follows an equation :

$$M = T(\mathrm{d}m/\mathrm{d}T)_p$$

where $m$ is the magnetic moment per unit mass produced by unit field, and $M$ the heat absorbed. The Heat Theorem gives :

$$\text{Lim } (M/T) = \text{Lim } (\mathrm{d}m/\mathrm{d}T)_p = 0 \text{ as } T \longrightarrow 0$$

The electromotive force of the Peltier effect is related to the Peltier heat by the equation :

$$Q = T(\mathrm{d}e/\mathrm{d}T)_p$$

and it is to be expected that :

$$\text{Lim } (Q/T) = \text{Lim } (\mathrm{d}e/\mathrm{d}T)_p = 0 \text{ as } T \longrightarrow 0.$$

All these equations agree with experimental results when these are available.

## Photochemistry

If light waves fall normally on a metallic mirror and are reflected, stationary waves are produced by interference, and Wiener (1890), by covering the mirror with a thin sensitive photographic film making a small angle with it, found that the antinodes of the electric waves appear as dark lines on the film. Drude and Nernst (1892) used a florescent film, which made the positions of the antinodes visible. These results were important in confirming that the vibration of the electric vector in light waves corresponds with Fresnel's vibration, and is perpendicular to the plane of polarisation.

[37] *J. Chim. phys.*, 1910, **8**, 228.

Modern photochemistry dates from Einstein's law of photochemical equivalence (1912), which states that a molecule undergoing photochemical change absorbs one energy quantum, $h\nu$, from the radiation in the primary photochemical process. The products of this primary reaction may then undergo secondary reactions not depending on illumination. Although Einstein's law was found to hold for many reactions, in the famous reaction on the study of which Bunsen and Roscoe founded photochemistry, the union of hydrogen and chlorine, $H_2 + Cl_2 = 2HCl$, at least a million molecules of HCl are formed per absorbed quantum, instead of two, as would be expected from the equation $Cl_2 + h\nu = 2Cl$. Nernst (1918) [38] explained this in a very simple and ingenious way. The absorbed quantum dissociates the chlorine molecule into atoms. A chlorine atom then reacts with a hydrogen molecule to form HCl and atomic hydrogen by a secondary process. The hydrogen atom in turn reacts with a chlorine molecule to form an atom of chlorine, which starts the process again :

$$Cl_2 + h\nu = 2Cl$$
$$Cl + H_2 = HCl + H$$
$$H + Cl_2 = HCl + Cl$$

This atomic chain is propagated until the active atoms are removed by collision with the walls of the vessel or with other particles, such as oxygen molecules, and the reaction stops. There is little doubt that this theory is, in principle, correct. Nernst published two papers with Noddack on photochemistry, and his pupil Eggert has been very active in this field.

In his later years Nernst had seen great changes brought about in the field of physical theory by the quantum theory and the theory of relativity. Laws of Nature which had been supposed to be accurately true had been shown to be approximations, and he inclined to the view that it may never be possible for us to know the ultimate truth of phenomena. In his lectures in London in 1913 he had quoted Shakespeare :

> " But this eternal blason must not be
> To ears of flesh and blood "

In his address as Rector of Berlin University in 1922 he developed this thought. A natural law is only idealised experience (*Erfahrung*), a lucky combination of a number of results of observation. The conviction grows on us that we do not possess a single natural law in a final form. The simplest among possible representations is to be preferred, not only because it is the most convenient but also because it is likely to be the most probable. A law which has been revised in the light of new knowledge still retains its wide range, but the limits of its applicability have been more sharply defined; and scientific theories, far from dropping off like withered leaves in course of time, seem, with certain restrictions, to be endowed with eternal life. Every important theory will suffer restrictions, but it will always retain the essence of a sum of truths.

Great changes had been made in the picture of the universe. The ether, which had played an important part in the development of optical theories in the nineteenth century, had disappeared and in its place was left only a vacuum. Nernst was conservative in theory. He retained the ether, and he was solicitous of the fate of the universe. He could not contemplate either the old heat-death of the universe, when all its energy will have changed into heat at a uniform temperature, or the newer, more gruesome death, in which all matter will have passed into radiation. His latest publications are concerned with astrophysical theories, and the energy of the universe. They have not found a place in the modern structure of astrophysics but they are so typical of him that a passing mention of them cannot be omitted. He began, as usual, by collecting and tabulating numerical data. The temperature in the early life of a star at first rises rapidly and then slowly falls to about 2000° K. Nernst assumed that new stars are being formed as giant nebulæ, and their mass continually decreases. Three sources of energy were assumed : (i) radioactive decay in the early period, (ii) atomic disintegration in the long subsequent period, (iii) gravitational energy when white dwarfs are formed with increase of density, perhaps by the formation of neutrons. The essential part of the theory is that the loss of mass is non-relativistic, there being no simultaneous production of radiation, since experimental evidence for this he thought was lacking. Matter and energy, however, are interconvertible. The universe is in a stationary state, matter being in equilibrium with an immense store of zero-point energy in the ether. Owing to fluctuations in the thermodynamic equilibrium state, the energy of the ether is transformed into atoms rich in energy. These

[38] *Z. Elektrochem.*, 1918, **24**, 335.

partly disintegrate, forming cosmic radiation, and partly coalesce to form fixed stars. The stationary state of the universe requires that matter must also pass back, non-relativistically, into the energy of the ether.

Although these speculations, the last fruits of his fertile imagination, are in themselves not without interest, they have had no influence on the rapid and fluctuating progress of modern cosmology. The same cannot be said of another contribution of Nernst in this field, which has played a very important part in the development of quantitative stellar theory.

In 1918 he pointed out that the chemical constant of the electron may be calculated by (37), and hence the thermal dissociation of an atom into a positive ion and an electron may be determined if the heat of dissociation is known. This could be found in some cases from the Bohr atom model. The detailed treatment of this phenomenon by Nernst's pupil Eggert in 1919, and independently by Saha in 1920, has proved to be of great importance in the calculation of temperatures and pressures in reversing layers of stellar atmospheres from observations on the intensities of absorption lines in the spectra. This is a particularly interesting and important application of the Heat Theorem, which was suggested by Nernst himself.

My duty in presenting a picture of Nernst and of his work is now ended. His contributions to Physical Chemistry are solid and I believe that they will endure. In physical chemistry, as in geology, time is a great leveller. Landscapes of theory dissolve and are replaced by newer formations overlying and concealing more primitive ones. Yet there are some hard and resisting primitive masses which appear, unconformably sometimes, projecting from the level of material derived from the comminution of old formations. In physical chemical theory such are, I think, the electrochemical and thermodynamic theories of Nernst. They offer themselves for our admiration.

In his time he was one of the great masters. To different individuals he would appear in various aspects. It was as a very young man, with little experience, that I spent a short time with him, and in my memory he remains a man of great intellectual power, but also something more. He took an interest in me which he showed in many ways. Soon after I arrived in Berlin, speaking German imperfectly, I was required to give a lecture to the Colloquium. This was carefully written out, but very soon he interrupted with criticisms and comments. The audience, knowing his ways, was quiet and attentive, and I finished without script. He saw that I lacked confidence and this was his treatment of the complaint. It was for my good and was meant kindly. My research was not easy, but even his presence, without words, was an incentive; one felt that he could do the work easily himself, and that perseverance would remove lack of skill, a fault which could be cured by application. If one visited his house, he might ask for an opinion of a picture, and I remember that he once asked my advice as to whether a tree in his garden should be removed. He would leave about publications by the visitor as if he wished it to be thought that he had read them. His true kindness is something I remember with gratitude, and I would like to leave you with such an idea of him. I feel that I am fortunate in having known him, and I value this opportunity to pay some tribute to his memory.

# *Discoveries among Conjugated Macrocyclic Compounds.*

THIRTEENTH PEDLER LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY AT BURLINGTON HOUSE ON THURSDAY, JANUARY 22ND, 1953, AND AT THE UNIVERSITY, ABERDEEN, ON THURSDAY, MARCH 12TH, 1953.

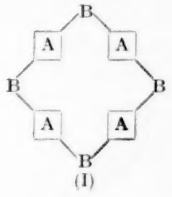
By R. P. LINSTEAD.

I MUST begin by defining my scope. The lecture will be concerned with macrocyclic compounds containing rings of 16 or more atoms with either perfectly conjugated or cross-conjugated systems of double and single bonds. There is no obvious geometrical reason why large conjugated rings of carbon atoms should not exist—why the *cyclo*octatetraene pattern should not, as it were, be extended—provided one is allowed latitude in the use of re-entrant angles and, if necessary, departure from planarity. However, such structures have not yet been substantiated, and the simplest conjugated macrocycles known to us are those in which four cyclic units A are joined by linking atoms B to make up the large ring (I). A and B must be of such a type as to permit conjugation.

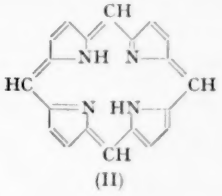
The group is of the highest importance. It includes chlorophyll, hæmin, and the other natural porphyrin pigments, whilst the widely distributed and vitally important iron-containing enzymes contain prosthetic groups based on the same structural pattern. In the space of a brief lecture, it is possible to look at only a few aspects of macrocyclic compounds, and I propose to survey the general range of their structures, the methods of synthesis, and certain aspects of their properties. Moreover, I shall speak mainly of the aza-linked macrocycles, where B is $-N=$, on which most of my own work in the field has been done.

The state of knowledge in 1930 can be roughly summarised in this way : the only important class of substances to which a conjugated macrocyclic structure had been given was the porphyrin group. For these the Küster formula, based on porphin (II) had been revived by Hans Fischer.[1] There was no rigid proof of this structure which rested largely on massive circumstantial evidence derived from the synthesis of various substituted porphyrins.

In 1927—1928 complex metallic compounds, subsequently recognised as derivatives of phthalocyanine, first came to light, the copper compound being made (although not identified) by de Diesbach and van der Weid [2] and the iron compound discovered in the Grangemouth factory of Imperial Chemical Industries Limited.[3] I started work on this group of compounds in 1929 at the Imperial College of Science and Technology. The parent compound, phthalocyanine, was soon synthesised [4] and the structural formula (III) was proposed in 1933.[5] Subsequently a considerable effort was devoted to proof of the constitution, examination of the chemical and physical properties, determination of the range of the structural type and of the



(I)



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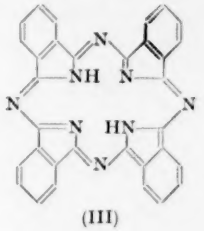


(III)

ability to form complexes with metals.[6] There will be no need to go into details of this early work, which has already been summarised.[7] For our present purpose I will merely draw two general conclusions from the work done up to 1936. First, phthalocyanines and many similar compounds were very easily prepared and were remarkably stable (indeed, as is well known, many of them are nowadays made on an industrial scale). It may be concluded therefore that conjugated macrocycles of this kind are inherently favourable structures, and the difficulty in preparing some of them, such as the porphyrins, is in a sense accidental and derives from the instability of intermediates. Secondly, the structure of phthalocyanine and of its metallic derivatives was proved with complete certainty. The chemical evidence [5] on which the

structure * (III) was first advanced was in itself conclusive, and received overwhelming support from the investigation carried out by J. M. Robertson by the *X*-ray method.[8] This moreover provided precise information on structural detail which was not otherwise available. Robertson's results may be illustrated by the electron density map for phthalocyanine shown in Fig. 1. The coincidence between the chemical and physical pictures of the molecule was summarised in an arresting phrase :[9] " This pattern may be said to provide the first purely physical demonstration of the truth of organic chemistry."

The rigid proof of a macrocyclic structure for the phthalocyanines invalidated the argument which had been used against the Küster formula for the porphyrins, namely, that it was of an unprecedented kind.

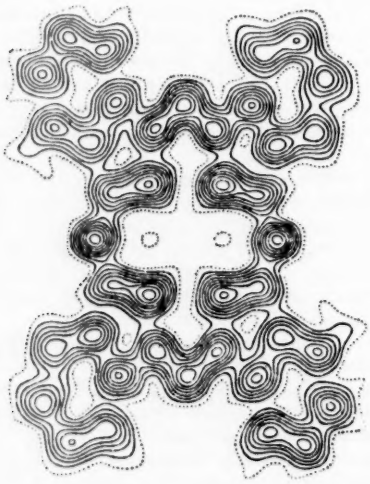
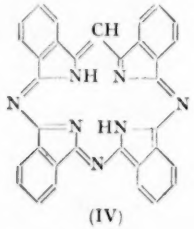


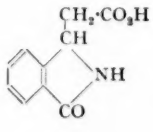
FIG. 1. *Metal-free Phthalocyanine* (J. M. Robertson).

*Electron density map. Projection along* b *axis. Each contour represents a density increment of one electron per* Å$^3$.

On the dual basis, therefore, that conjugated macrocyclic structures were stable and were certain, it was possible to advance with confidence. Much further work at the Imperial College has been done in two directions : first, an examination of the range of the porphin and azaporphin type of pigment exemplified by (II) and (III) ; secondly, an exploration of the possibility of making conjugated macrocycles of quite different kinds. Good progress has now been made in both fields, and I shall deal with them in turn.



(IV)



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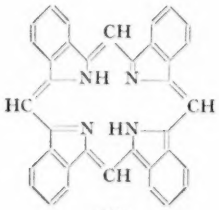


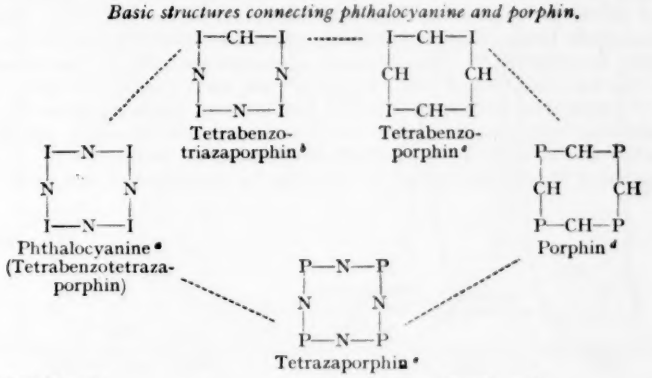
(VI)

An immediate objective was of course to bridge the gap between phthalocyanine and porphin itself. As the chart shows, this could be done in two ways—by keeping the *iso*indole units of phthalocyanine and linking them by methene groups instead of by nitrogen atoms or by keeping the nitrogen links and replacing the *iso*indole corners by pyrrole nuclei. In the next period (1936—39) most success came from the *iso*indole compounds. We were able to prepare compounds with one methene and three nitrogen,[10] with one nitrogen and three methene, and

* Certain points of fine structure remain to be settled : for example, the mode of attachment of the two central hydrogen atoms, and the possibilities of tautomerism. This is a general residual problem in the group of tetrapyrrolic pigments.

with four methene links.[11] I will illustrate the rather unconventional methods used. If phthalonitrile is treated with methylmagnesium iodide or methyl-lithium it gives a product which when heated at 200° with a hydrogen donor gives magnesium tetrabenzotriazaporphin (IV) in about 40% yield.[10] The best intermediate for tetrabenzoporphin is 3-oxo*iso*indolin-1-ylacetic acid (V); when this is heated at 450° with zinc acetate it gives zinc tetrabenzoporphin (VI) in 15% yield.[11] The structures of these substances were established by chemical, supported by spectroscopic, evidence; moreover J. M. Robertson [12] showed that the triaza-compound (IV) was strictly isomorphous with phthalocyanine. Similar investigations were carried out independently by Helberger and his associates in Berlin.[13]

***Basic structures connecting phthalocyanine and porphin.***



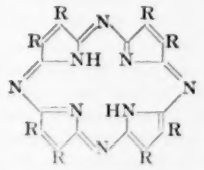

I = *iso*Indole unit. P = Pyrrole unit.

[a] Byrne, Linstead, and Lowe, 1934. [b] Barrett, Linstead, and Tuey, 1939. [c] Barrett, Linstead, Rundall, and Tuey, 1940. [d] Fischer and Gleim, 1936. [e] Linstead and Whalley, 1952.

On the other hand, progress towards tetrazaporphin and simple derivatives was very limited during the pre-war period, and in particular various attempts to prepare the necessary dinitrile of maleic acid failed to yield us a satisfactory product. The related diphenyl derivative, dicyanostilbene (VII), was however obtained and shown to yield macrocyclic pigments of the desired type, namely octaphenyltetrazaporphin (VIII; R = Ph) and its metallic derivatives.[14] Incidentally, it now appears that the key intermediate (VII) may have the *trans*- and not the *cis*-configuration, as has previously been supposed.[15] During the same period, and using quite different methods, Hans Fischer and his collaborators described the preparation of "imidoporphyrins" [16] and in particular tetraimido*ætio*porphyrin.[17] The absorption spectrum of this compound was almost identical with that of compounds recently prepared in my laboratories, which undoubtedly have the structure (VIII) where groups R are alkyl or part of a polymethylene ring.

NC·CPh = CPh·CN

(VII)



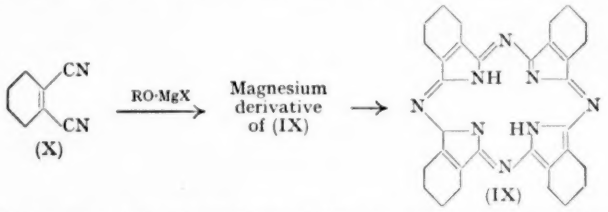
(VIII)

When I was able to resume investigations of azaporphins three years ago attention was again directed to the preparation of tetrazaporphin (VIII; R = H) itself and of its tetra*cyclo*hexeno-derivative (IX). By this time authentic maleic nitrile had been reported in the literature, although its preparation was still difficult, and an important advance had been made by chemists of the Dyestuffs Division of Imperial Chemical Industries Limited (1949—50).[18] They showed that when maleic nitrile or 3 : 4 : 5 : 6-tetrahydrophthalonitrile was heated with a metallic reagent, urea, and ammonium molybdate, a highly coloured pigment was obtained. From the method of preparation and general properties these were formulated as metallic tetrazaporphins.

In our investigations of these two dinitriles we have concentrated upon their conversion

into tetrazaporphin derivatives containing a labile metal. In this way a route was opened to the metal-free compound which could subsequently be converted into any desired metallic derivative. Dr. M. Whalley in my laboratories has successfully solved the delicate problems of the routine preparation of maleic nitrile and from it of magnesium tetrazaporphin. This is best made by the action of magnesium *n*-propoxide on the nitrile. The yield is about 20% and the product is readily purified by chromatography. The metal is eliminated by cold glacial acetic acid wthout destruction of the macrocycle.[19]

The corresponding compounds in which the β-carbon atoms of the pyrrole ring are substituted are more easily obtained, both the intermediates and the macrocycles being more stable. Dr. Ficken has found that 3 : 4 : 5 : 6-tetrahydrophthalonitrile (X) on treatment with a reagent formed by the decomposition of methylmagnesium iodide with amyl alcohol gave a 66% yield of magnesium tetra*cyclo*hexenotetrazaporphin, from which the metal-free compound (IX) could readily be obtained.[20] The structure of compound (IX), a hexadecahydride of phthalocyanine, has been established with certainty,[20] the main pieces of evidence being that (i) the method of preparation corresponds to the formation of phthalocyanine from phthalonitrile, (ii) two atoms of hydrogen are present which are replaceable by metal, (iii) the molecule undergoes oxidative fission to 3 : 4 : 5 : 6-tetrahydrophthalimide and ammonia, and (iv) it is readily dehydrogenated to phthalocyanine, for example, by the action of heat at about 300°.



(X) (IX)

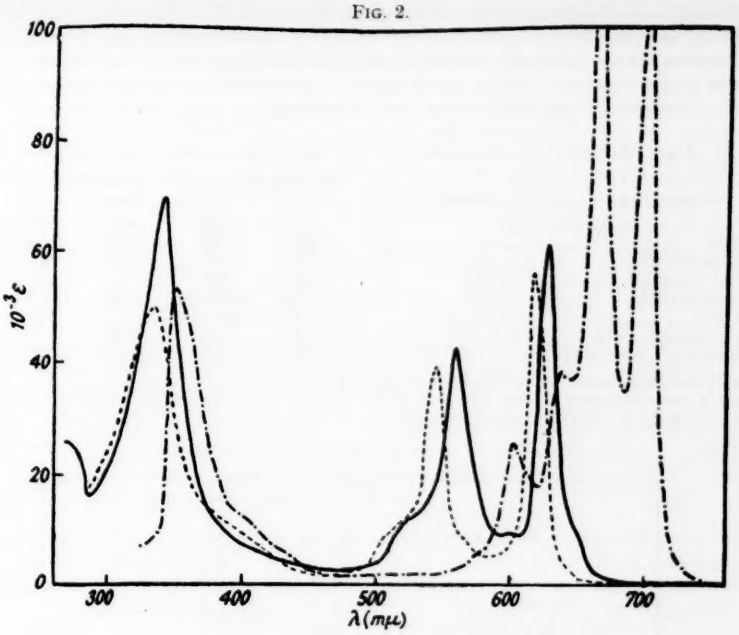
In the case of tetrazaporphin, the evidence of dehydrogenation was not, of course, available and, whilst the oxidative fission gave ammonia, the maleinimide was too unstable for isolation under the conditions of reaction. Hence only (i) and (ii) of the above lines of evidence were available. Fortunately, convincing spectroscopic evidence confirmed the structure (VIII; R = H). This is described later. The structures of the new tetrazaporphins can be regarded as firmly established.

In summary, therefore, the range of tetrapyrrolic conjugated macrocycles has now been greatly extended. Research in progress at the moment has led to further improvements in preparative methods and to the discovery of tetrazaporphins with unsymmetrical arrangements of the corner units.

I should next mention some of the remarkable and characteristic properties of the tetrazaporphins. First, the absorption of light in the visible and the ultra-violet region. This may conveniently be reviewed in comparison with that of the porphyrins. In the visible region all the simple * metal-free porphins and azaporphins have a multibanded absorption spectrum in the blue-green to vermilion region, between about 500 and 620 mμ. If benzene or similar rings are fused to the pyrrole nuclei the region of absorption is extended into the red, up to about 700 mμ. This is illustrated in Fig. 2. The intensity of the absorption is very greatly increased when the methene links of porphin are progressively substituted by nitrogen atoms (Fig. 3). This is shown particularly by the first band of the simple porphins and azaporphins which lies in the region of 620 mμ. The measurements made by Stern and Pruckner on the compounds prepared by Hans Fischer and his collaborators provide good evidence on this point in the series *ætio*porphyrin–tetraza*ætio*porphin.[21] Now, among the simple tetrazaporphins, the structure of the tetra*cyclo*hexeno-derivative (IX) has been conclusively proved by the chemical evidence summarised above. It is therefore of particular importance that the light absorption of this compound is found [20] to be virtually identical with Stern and Pruckner's measurements on tetraza*ætio*porphin (Fig. 4). This substantiates the structure of the tetraza- (tetraimido-)-materials made by the Münich school and links their work with ours. It is equally important that tetrazaporphin itself has a light absorption in the visible and near ultra-violet region very closely resembling that of the tetra*cyclo*hexeno-derivative (Fig. 2).[19, 20] There is a corresponding close resemblance between the spectra of corresponding metallic derivatives [19, 20] (Fig. 5). This puts the structure of tetrazaporphin on a firm basis.

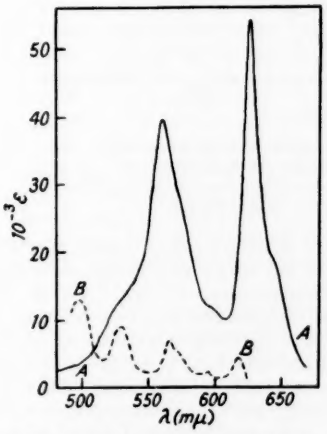
* *I.e.*, those without fused rings.

FIG. 2.



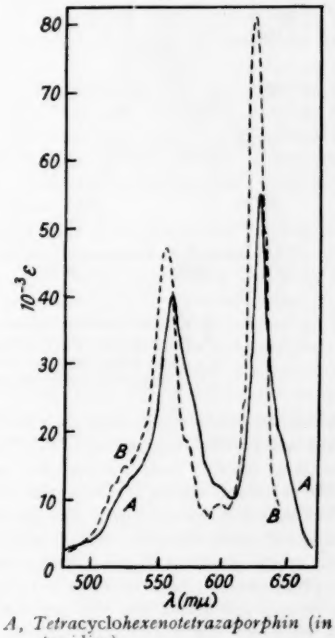

——————— *Tetracyclohexenotetrazaporphin (in chlorobenzene).*
– – – – – – – *Tetrazaporphin (in chlorobenzene).*
— · — · — *Phthalocyanine (in chloronaphthalene).*

FIG. 3.




*A, Tetracyclohexenotetrazaporphin (in pyridine).*
*B, æTioPorphin-II (in dioxan).*

FIG. 4.




*A, Tetracyclohexenotetrazaporphin (in pyridine).*
*B, Tetrazaætioporphin (in pyridine).*

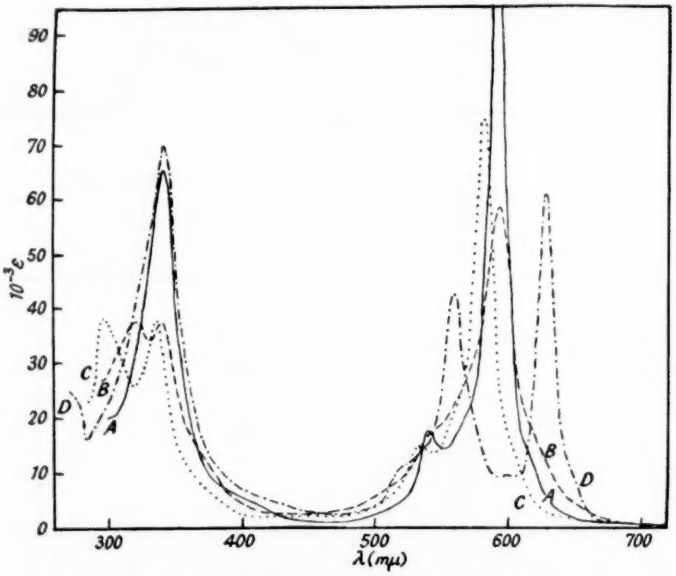
Table 1 summarises important data, taken from Stern's work [21, 22] and our own,[19, 20] on the positions of the maxima in the visible region. It will be seen that there are some grounds for saying that the bands appear in approximately the same positions throughout, only the intensity varying with substitution of nitrogen for methene. This is evident enough for band I but the position is less clear-cut in the bands of shorter wave-length, in the green region.

TABLE 1. *Light absorption in the visible region of metal-free porphin and azaporphins.*

| Compound | Band | Maxima of absorption bands (mμ) IV | III | II | Ia | I | Ref. |
|---|---|---|---|---|---|---|---|
| Porphin | | 490 | 518 | (561) | (602) | (613) | 1 |
| *ætio*Porphyrin | | 497 | 529 | (566) | (596) | (619) | 1 |
| Monoaza*ætio*porphyrin | | 501 | 534 | 560 | (588) | 610 | 1 |
| βδ-Diaza*ætio*porphyrin | | — | 543 | (569) | — | *620* | 1 |
| Tetraza*ætio*porphyrin | | — | (526) | *556*(573) | (599) | *624* | 1 |
| Tetrazaporphin | | — | (510) | *545*(565) | — | *617* | 2 |
| Octamethyltetrazaporphin | | — | (525) | *556* | (597) | *627* | 2 |
| Tetra*cyclo*hexenotetrazaporphin | | — | (525) | *560* | (600) | *628* | 2 |

Strong bands italicised; weak bands in parentheses.
[1] Stern's measurements on compounds of H. Fischer *et al.* (pyridine solutions). [2] Linstead, Whalley, and Ficken (chlorobenzene solutions).

FIG. 5.




*A, Copper tetra*cyclo*hexenotetrazaporphin (in dichlorbenzene).*
*B, Nickel tetra*cyclo*hexenotetrazaporphin (in dichlorbenzene).*
*C, Palladium tetra*cyclo*hexenotetrazaporphin (in dichlorbenzene).*
*D, Tetra*cyclo*hexenotetrazaporphin (in chlorobenzene).*

In addition to their visible selective absorption, all these macrocycles have an intense band in the near ultra-violet region, which (in the case of the porphyrins themselves) is generally called the Soret band. This is shown for various tetrazaporphins in Figs. 2 and 5. The Soret band differs from the visible bands in the effect of the introduction of nitrogen links. Whereas the first visible band (for example) changes enormously in intensity but hardly at all in position, the ultra-violet band changes considerably in position but hardly at all in intensity. The evidence is summarised in Table 2, from which it is seen that the maximum of the Soret band for porphyrins lies at about 400 mμ with log $\varepsilon_{max.}$ about 5·1. For tetrazaporphins the corresponding figures are about 340 mμ and 4·9. One consequence is that the ultra-violet band is much the strongest for porphyrins whereas in the tetrazaporphins the strongest visible bands are of comparable intensity.

Replacement of the two acidic hydrogen atoms of tetrazaporphins by an atom of bivalent tetraco-ordinate metal leads to a simplification of the light absorption in the visible region. The effect can be summarised by saying that the two strong bands (λ *ca.* 627 and 558 mμ in a substituted tetrazaporphin) are replaced by an intense band of intermediate wave-length (*ca.* 590 mμ) with a weak band or inflexion on the short-wave side (*ca.* 545 mμ). As will be seen, for example, in Fig. 5 the nature of the metal affects the intensity but only to a minor

TABLE 2. *Effect of linking groups in simple tetrapyrrolic pigments on the intensities and positions of the first bands in the ultra-violet and the visible region.*

| | Ultra-violet | | Visible (band I) | | |
|---|---|---|---|---|---|
| Linking groups | λ | log $\varepsilon_{max.}$ | λ | log $\varepsilon_{max.}$ | Ref. |
| 4 CH, no N | 398—405 [a] | 5·05—5·24 [a] | 622 | 3·76 | 1 |
| 3 CH, 1 N | 376 | 5·06 | 610 | 4·43 | 1 |
| 2 CH, 2 N | 373—375 [a] | 5·01—5·16 [a] | 620 | 4·67 | 1 |
| no CH, 4N | 333—343 [a] | 4·70—4·98 [a] | 617—628 [a] | 4·75—4·79 [a] | 2 |

[a] This denotes the range of values encountered in representative compounds of the class.
[1] Stern's measurements on compounds of H. Fischer *et al.* (pyridine solutions). [2] Linstead, Whalley, and Ficken (chlorobenzene solutions).

extent the position of the main visible band. The first ultra-violet band of the tetrazaporphins is also present, not much changed in position, in their metallic derivatives. There is some variation in intensity with the nature of the metal and in a few cases the bands are divided into two.[19, 20] This is illustrated in Fig. 5 and in Table 3.

TABLE 3. *Effect of central metal on the ultra-violet absorption of some tetrazaporphins.*[20]

| Nature of metal | | None (metal-free) | Mg | Co | Ni | Cu | Pd |
|---|---|---|---|---|---|---|---|
| Tetra*cyclo*hexenotetraza-porphin | $\lambda_{max.}$ | 343 | 344 | 350 | 342 | 343 | 338 |
| | log $\varepsilon_{max.}$ | 4·84 | 4·96 | 4·67 | 4·57 | 4·81 | 4·58 |
| Phthalocyanine | $\lambda_{max.}$ | 350 | 347 | — | 351 | 350 | 347 |
| | log $\varepsilon_{max.}$ | 4·74 | 4·73 | — | 4·57 | 4·76 | 4·69 |

Many of the regularities noted above are reproduced among the more complex structures in which rings such as benzene are fused to the porphyrin or azaporphin system. A noteworthy effect is the bathochromic shift of about 80 mμ in the main visible bands caused by the fusion of four benzene rings to the pyrrole nuclei when we pass from tetrazaporphins to phthalocyanine. This is accompanied by a great intensification of absorption in both the metal-free and the metallic derivatives.[11, 23]

Haurowitz [24] regards the visible band system of the porphyrins as representing different vibrational bands corresponding to one electronic transition, and the Soret band as due to a separate electronic transition. This is in keeping with the small effect of structural modifications (including the introduction of metal) on the Soret band compared with their considerable effect on the system of bands in the visible region. The same phenomena occur among the tetrazaporphins and may be attributed to the same causes.

It is worthy of note that tetrazaporphin has a normal absorption spectrum [19] which resembles that of its alkyl derivatives (Fig. 2 and Table 1). The position is different for porphin, the parent substance of the porphyrins. This is a rare compound, for which the only reported preparations are those by Fischer and Gleim [25] and by Rothemund.[26] Fischer's material had a " phyllo "-type of spectrum [22] rather than the normal " ætio "-type illustrated in Fig. 3. This means that although the four main visible bands are more or less in the normal position, the intensity of band II is greater than that of band III. There seems no obvious reason why the alkylation should produce a different effect in the tetraza- and the tetramethene series and a reinvestigation of porphin is desirable. In Rothemund's preparations the position is more obscure owing to the presence of material at different hydrogenation levels, as Aronoff and Calvin have shown.[27]

Among all these tetrapyrrolic compounds the phthalocyanines possess particularly sharp and intense absorption bands in the visible region and, as they are also remarkably stable, they function as brilliant and stable pigments of technological value. By suitable substitution the chemists of Imperial Chemical Industries Limited have been able to convert them into water-soluble dyes capable of application to textiles.

I turn next to the fluorescence of the tetrazaporphins. The experimentalist working with these materials soon becomes aware that some, but not all, of them show a vivid fluorescence when exposed to visible or ultra-violet light. This is best shown by the magnesium compounds.

It was observed for magnesium phthalocyanine and magnesium octaphenyltetrazaporphin before the war [14] and had long been known for the chlorophylls.[28] More recently we have observed that magnesium derivatives of tetrazaporphin and its alkyl derivatives fluoresce brilliantly when exposed to visible or ultra-violet light.[19, 20] The results may be exemplified by the tetra*cyclo*hexenotetrazaporphin series. The parent compound shows a weak visible fluorescence and a strong rose-red ultra-violet fluorescence, whilst its copper, nickel, and cobalt derivatives virtually do not fluoresce. The fluorescence of the magnesium compounds is shown by solutions in pyridine, alcohol, or dioxan; it is red in visible light, vermilion in ultra-violet light. Solutions of the magnesium compound in benzene or chlorobenzene show practically no fluorescence but the addition to these of a drop of alcohol or pyridine at once activates the fluorescence.[20, 29] These results at once recall those of Livingstone and his collaborators [30] on the activation of the fluorescence of chlorophyll and we in fact find that there is a general agreement between the two series in the nature of the activators and in the rough order of their effectiveness. In considering the relation of these properties to structure, two pieces of evidence are relevant. First, the metal-free tetrazaporphins show no similar activation; secondly, the magnesium derivatives of phthalocyanine and of the new tetrazaporphins have the property (unusual among metallic azaporphins) of crystallising in solvated forms containing molecules of water, alcohol, or base. We therefore agree with Evstigneev, Gavriola, and Krasnovskii [31] in attributing the activation of fluorescence to a process involving the co-ordination of the central magnesium atom with the activating solvent, a proposal which has recently been accepted by Livingstone and Weil.[32]

The similarity between chlorophyll and the magnesium azaporphins also extends to the quenching of their fluorescence. We find [29] that substances such as nitro-compounds and quinones powerfully suppress the fluorescence of magnesium tetra*cyclo*hexenotetrazaporphin and that the order of quenching by different agents is very similar to that observed by Livingstone and Ke.[33] Among quinones the quenching efficiency roughly follows the redox potential, quinones of high potential having the largest effect.

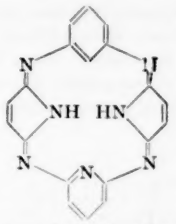
I must also refer briefly to the catalytic properties of metallic tetrazaporphins first investigated by A. H. Cook.[34] Amongst these the most striking is the decomposition of the peroxides contained in aged samples of terpenes and similar hydrocarbons by means of magnesium phthalocyanine and similar compounds. This occurs at temperatures of about 180° and is accompanied by a vivid red chemiluminescence. The effect is also shown by chlorophyll. We have now found that it is given by magnesium tetrazaporphin, so that it is presumably connected with the presence of a magnesium atom bound to four nitrogen atoms in the macrocyclic environment, although we do not yet know how many of these structural factors are obligatory.

*Conjugated Macrocycles of Other Types.*—It is evident that what may be called the tetrapyrrolic type of large ring structure is capable of fairly wide variation, and that compounds possessing it are often easily prepared, very stable, and striking in their properties. The question arises as to whether it is possible to branch out from this structure into new types of conjugated macrocycles. We can indeed construct on paper a considerable number of tolerably plausible formulæ. But in this lecture I will confine myself to a group of compounds in which such speculative blue-prints have been converted into experimental fact and in which the resulting structures can be regarded as fully established.

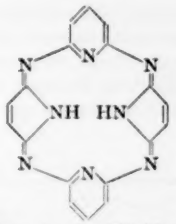
As indicated earlier, the known conjugated macrocycles (formula I) contain four corner units, A, held together by linking atoms, B, all the known A units being pyrrole or fused pyrrole rings. An inspection of formulæ (II) and (III) shows that one canonical structure has one true pyrrole ring, two pyrrolenine rings, and one ring of a maleinimide type. If now two of the pyrrole groups are replaced by benzenoid or pyridine rings, we arrive at compounds such as (XI) and (XII). Such structures do not violate our general conceptions of molecular geometry, and there seems to be no *a priori* reason why they should not be realisable. Nevertheless certain differences from the azaporphin type follow the introduction of the six-membered rings as building units, and in particular the symmetry and conjugation of the system are altered. In the tetrazaporphin molecule the central hydrogen atoms can be accommodated with equal (or nearly equal) convenience on any two of the pyrrole rings, and similarly in their metallic derivatives the metal can be attached by primary valencies to any two of the pyrrole nitrogen atoms.* If we examine the pyridine-containing macrocycle, the formula (XII), with the

* The interesting question as to the degree of sharing of the metal or of the two central hydrogen atoms between the pyrrole nitrogen atoms, and the consequential degree of degeneracy of the system, must be passed over in this lecture.

central hydrogen atoms on pyrrole nitrogen, is inherently more probable than the isomeric form in which the hydrogen atoms are carried on the pyridine nitrogen, and we may expect that (XII) would make a much larger contribution to the structure. If the pyridine rings remain aromatic then the other double bonds will take up the positions shown in (XII). The macrocycle is thus cross-conjugated, and not fully conjugated as in tetrazaporphin (VIII; R = H). These arguments of course would apply *a fortiori* to the benzenoid macrocycle (XI). It will be noted, however, that the pyridine macrocycle (XII) resembles tetrazaporphin in having the four re-entrant nitrogen atoms with two hydrogen atoms in a position suitable for formation of metal complexes. In summary, therefore, we would expect compounds (XI) and (XII) (*a*) to be capable of existence, and (*b*) to resemble the tetrazaporphins in many respects, but (*c*) to differ from them in those properties derived from the full conjugation of the molecule, such as the light-absorption properties. The pyridine, but not the benzene, macrocycle would form metal complexes. There will also be differences in the mechanism of fission, which are mentioned later.

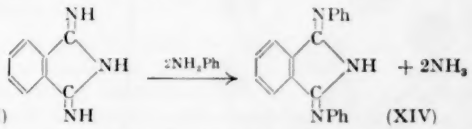



(XI)




(XII)

About two years ago investigations with Dr. J. A. Elvidge opened up a line of experimentation by which these structures might be approached. Work at the Imperial College [35] and in the laboratories of Imperial Chemical Industries Limited [36] and of the Bayer Company [37] had led to the preparation of di-imino*iso*indoline (XIII) both as the free base and in the form of its salts. This readily available and highly interesting compound has, we find, a number of ready modes of reaction. For our present purpose the important one is that it combines with primary amines with evolution of ammonia and the formation of *N*-substitution products. The reaction with aniline is typical :




(XIII) (XIV)

It was therefore obvious that reaction of di-imino*iso*indoline with a suitable diamine might give rise to a macrocycle through a series of condensations of this kind.

This possibility was first tested [35] using aminopyridines as the secondary component because this would permit the use of metal complexes to keep the molecule in a stereochemically favourable form. In fact, however, as will be seen, this was an unnecessary precaution. It was first found that 2-aminopyridine reacted readily with di-imino*iso*indoline in boiling butanol, to give ammonia and the dipyridylimino*iso*indoline (XV). The structure of this was proved by its easy hydrolysis to phthalimide and 2-aminopyridine. With 2 : 6-diaminopyridine in place of the monoamine a sparingly soluble orange-red crystalline product was obtained in some 40% yield. This substance has been conclusively proved to have the macrocyclic structure (XVI). The evidence is briefly as follows : [35] (*a*) Analysis of the red compound corresponds to $C_{13}H_8N_4$ and the molecular weight to double this. Hence the preparative reaction is :

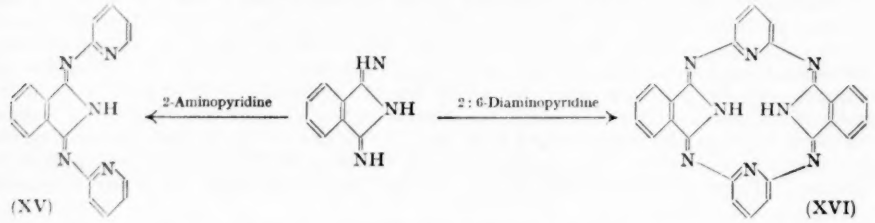
$$\underset{\text{Di-imine}}{2C_8H_7N_3} + \underset{\text{Diamine}}{2C_5H_7N_3} = \underset{\text{Macrocycle}}{C_{26}H_{16}N_8} + 4NH_3$$

(*b*) On treatment with acid the compound yielded equivalent amounts of phthalimide and 2 : 6-diaminopyridine. No oxidation was involved, as in the fission of a phthalocyanine or tetrazaporphin. The reaction is :

$$C_{26}H_{16}N_8 + 4H_2O = 3C_8H_5O_2N + 2C_5H_7N_3$$

This hydrolysis shows the presence of the intact pyridine and *iso*indole rings which must be linked together by extranuclear nitrogen atoms. Moreover, these units must be alternate as

otherwise diaminopyridine could not be re-formed. These facts can only be explained on the basis of formula (XVI). Any linear counterpart would have end groups which would be detectable by elementary analysis or on fission or both. (*c*) The macrocycle extracted metals from their salts with the formation of complex metallic derivatives of the type shown below




The nickel compound (XVII), for example, was prepared [35] when the macrocycle in nitrobenzene was treated with nickel acetate in formamide. It melted at 386° and sublimed at about 300°/$10^{-5}$ mm., both without decomposition. The colour was a brownish-green and the absorption spectrum considerably changed from that of the parent compound. The hydrolysis products were nickel ion and the same organic compounds as were produced from the metal-free compound.

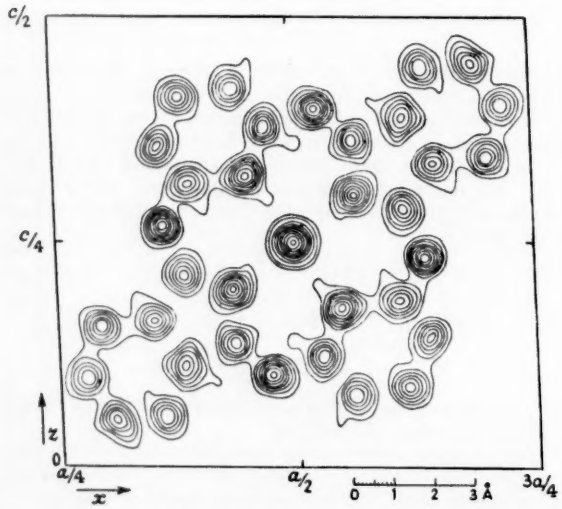
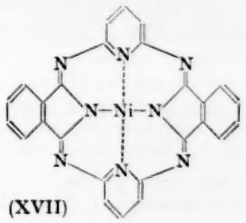



FIG. 6. *Nickel compound* (XVII). *Electron density projected along* b-*axis.*

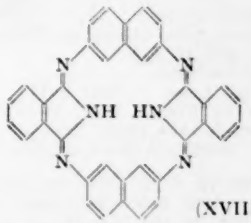
Dr. J. C. Speakman [38] of the University of Glasgow has investigated the crystals of the nickel compound by the *X*-ray method and has very kindly allowed me to report his findings. The crystals presented a very favourable case for analysis because the unit cell has one very short axis (which implies that a good projection of the structure should be attainable) and the nickel atoms are in special positions. The heavy-atom method, used with such effect by Robertson for the metallic phthalocyanines, could therefore be applied, although the relative smallness of the crystals made it difficult to obtain accurate intensity data. The structure represented by formula (XVII) is confirmed by the *b*-axis projection of the electron density. This is shown in Fig. 6. The molecule (in the crystal, at any rate) is however not planar, as were those of the phthalocyanines. Instead the nickel atom lies on a two-fold axis of symmetry, the eight nitrogen atoms are approximately co-planar with it, and the *iso*indole rings are tilted out of this plane by about 25° in one direction whilst the pyridine rings are similarly tilted in the other direction. The approximate molecular configuration is illustrated in Fig. 7.

Research into this new type of macrocycle is being extended by Mr. P. F. Clark to other aromatic and heterocyclic series, and we find that a considerable range can be obtained.[39] For example, we have replaced the pyridine groups of (XVI) by benzene, naphthalene, and acridine

units. The naphthalene macrocycle (XVIII) is particularly easily obtained, as it is formed in about 70% yield when 2 : 7-diaminonaphthalene is heated with di-iminoisoindoline. It is noteworthy alike for its central cross-conjugated great ring of 20 atoms and for its stability.




(XVII)




(XVIII)

Its melting point is in the region of 500° and it can be sublimed without decomposition at about 400°/15 mm. It resists the action of aqueous alkali and of boiling concentrated hydrochloric acid. As would be expected it fails to form complex metallic derivatives.

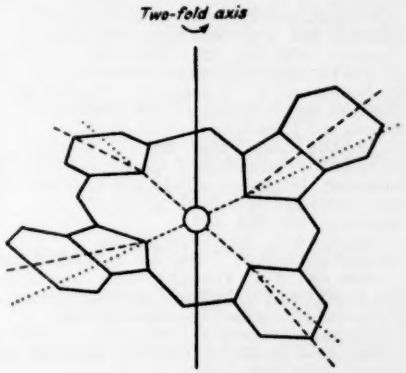



FIG. 7. *Nickel compound* (XVII). *Approximate molecular configuration in crystal.*

Because of the departure from complete conjugation, the new type of macrocycle shows a very different type of light absorption from the azaporphins. Thus the metal-free pyridine compound (XVI) has two strong bands but these are well in the ultra-violet region (λ 301, 354 mμ in morpholine), and there is only end absorption in the visible region. The colour is accordingly orange. The metallic derivatives have markedly different spectra. In particular the nickel derivative has a complex multibanded spectrum with one strong maximum in the visible region (λ 440 mμ, ε 35,800, in dimethylformamide). The introduction of metal has a far greater effect than in the azaporphin series; we attribute this to the fact that in the new type of macrocycle the metal increases the degree of resonance and the participation of forms other than the main structure (XVI), whereas this is not true for the azaporphins.[35]

The Pedler Lecturer is charged with the duty of pointing out those directions in which further research is desirable. I can interpret this in a narrow and in a wide way. From the narrow point of view these seem to be the most interesting and fruitful lines of further investigation of the macrocycles: First, much remains to be done on the exploration of the possible range of structure. Secondly, we need to rationalise the reactions, often obscure, by which azaporphins and porphyrins are formed; and as a pendant to this the mechanism of the remarkable easy biosynthesis of porphyrins is of exceptional interest. Thirdly, the catalytic properties and oxidation–reduction behaviour of macrocycles provide a most interesting field. Fourthly, many problems of fine structure remain to be settled.

There is also a wider issue which may be touched on. In organic chemistry today there is, quite rightly, very great activity in the fields of natural products, in the determination of the mechanisms of reactions, and in the refinement of the interpretation of known structures. But all this should not blind us to the fact that large tracts of organic chemistry still remain completely unexplored and that we are far from finality in our knowledge of the various manners in which carbon, hydrogen, oxygen, nitrogen, and the other hetero-atoms can combine and the

consequences of these combinations. The discoveries among the macrocycles which I have touched on today provide only a few examples of the rich structural jewels which still await the explorer.

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[5] Linstead, *Brit. Assocn. Reports*, 1933; Dent, Linstead, and Lowe, *J.*, 1934, 1033.
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